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PHILIPPINE TERPENES AND ESSENTIAL OILS, III.

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In endeavoring by a general survey to ascertain the economic possibilities of the Philippines in the field of terpenes and essential oils, I have found it convenient to plan the work in accord with the available material. This has made it necessary to leave many interesting oils when their study has been only well started, as the raw material is often available but once a year. The important factors of yield per hectare, the best time for harvesting, the effects of various soils, etc., must be ascertained on some of the perfume plants by slow experiments in the laboratory garden before reliable statements can be made as to the economic possibilities of these plants in the Philippines. In the present paper I present under separate subheads, the results obtained during the past year in this field. In all cases where the plant offers commercial promise the work is being continued as fast as new material is available.

MANILA ELEMI.

INTRODUCTION.

A. M. Clover [1] has published the results of the examinations of the terpene oils from twenty-one authentic samples of Manila *elemi* and he thus was able to isolate pure specimens of *d*-limonene, *d*-phellandrene, dipentene, terpinene, and terpinolene. I have continued this investigation and have collected over one hundred specimens of *elemi* from

[1] *This Journal, Sec. A.* (1907), **2**, 1.

individual trees, together with botanical material corresponding to each specimen.

In spite of the very careful work on this subject, published from this laboratory, the recent literature still abounds with inaccurate statements as to this resin, especially as to its source. Tschirch [2] in his handbook, states, "Das Manila Elemi stammt von *Canarium commune*," and again,[3] "Es darf jetzt als festgestellt betrachtet werden, dass das Manila Elemi von *Canarium commune* L. stammt." He also remarks that the tree is called by the Tagalogs *abilo*, a name which I find is wholly unknown to natives in the districts where *elemi* is collected. The native name for the tree is *pili*. Semmler [4] in discussing Manila *elemi* states that it is now well established that the resin is a product of the tree *Canarium commune* L. There is little doubt but that in India and Java a resin very similar to Manila *elemi* has as its source *Canarium commune* L., but for the Philippine *elemi*, the source has been definitely shown by Merrill to be *Canarium luzonicum* A. Gray.[5]

Tschirch [6] divides Manila *elemi* into three classes, (*a*) soft *elemi*, (*b*) hard *elemi*, (*c*) Tacamahac *elemi*. He speaks of the hard *elemi* as containing from 7 to 8 per cent of essential oil as compared with about 30 per cent for the soft variety and he gives the following constants for the two classes:

	Soft elemi.	Hard elemi.
Acid number, direct	19.6	22.4
Acid number, indirect	22.4	25.2
Saponification number, cold	29.4	30.8
Saponification number, hot	33.6	37.8

Manila *elemi* as it exudes from the trees is always soft. When it has remained on the trees exposed to the sun and air for several months it loses the greater part of its volatile constituents through evaporation and polymerization and becomes quite hard. There is no difference in the source of the *elemi*, the so-called hard *elemi* simply being more resinified by the action of the elements. There is but one *elemi* gum collected in the Philippines. While there are many species of *Canarium* in the Islands, only *Canarium luzonicum* yields an *elemi*-like resin in sufficient quantities to render its collection profitable. Tschirch gives such meager data regarding the Tacamahac *elemi* that it is impossible to identify it. It may possibly be the resin known in the Philippines as *pagsainguin* from *Canarium villosum* F.-Vill. This resin occurs in considerable quantities, but is always black or very dark, contains as the principal constituents of its volatile oil pure cymol, it does not have

[2] Die Harze and die Harzbehälter (1908), 424.

[3] *Loc. cit.*, 427.

[4] *Ber. d. deutschen chem. Ges.* (1908), **41**, 1768.

[5] The source of Manila *Elemi*, *Gov. Lab. Pub.*, Manila (1905), **29**, 51 to 55.

[6] *Loc. cit.*

the same odor as *elemi,* and would hardly be confused with true Manila *elemi* by anyone familiar with these resins. It is also possible that Tschirch's resin is the dipterocarpous resin from *balao* or *apitong* which in appearance is deceptively like *elemi,* but which has a decidedly different odor and the volatile oils of which are sesquiterpenes rather than terpenes.

The present condition of the Manila *elemi* industry is not very satisfactory. In several localities, especially in Tayabas Province in the neighborhood of Atimonan, the trees are regularly tapped and in past times the collection of *elemi* was one of the important industries of this province. The trees are usually owned in small holdings. The Bureau of Forestry assesses the trees at 50 centavos each and all minor forest products, such as resins, pay a tax of 10 per cent of their value at the place of collection. The resin is bought up by the small Chinese traders who then ship it to Manila. In recent years these Chinese traders have shown no eagerness to buy *elemi,* so that the native is either not able to sell his product at all or must accept a very small price for it. This price, since the collectors are a very primitive and ignorant class of men, naturally varies much with the personal needs and desires of these natives. In Calaoag, Tayabas Province, clean, white, fresh *elemi* is valued at 40 centavos per arroba of 11.5 kilos. When it is transported to Atimonan, Tayabas, 35 kilometers distant, it has a value of 1 peso for the same quantity and by the time it has reached Manila its value has risen to about 3 pesos. The market value in Europe is several times this amount. I quote these figures because they are typical of the condition under which all minor, tropical forest products are marketed. The native collectors usually live in the forests entirely out of touch with civilization, and know nothing of the real value of the products which they handle. Some of the resin is shipped from Manila to Europe for use in medicinal ointments, and to a smaller extent in lithographic inks, and in varnishes, while much of the product is sent to China, where it is used to make transparent paper to be employed for window panes, in place of glass.

The resin flows in the bark principally at the time when new leaves are coming out on the trees. This occurs most abundantly about the months of January and of June in the great collecting district around Atimonan, Tayabas. At other times of the year, when the tree is losing its leaves, it is not possible to obtain a flow of resin. The natives hack the tree with *bolos,* and the resin flows out through the cuts and collects on the bark of the trees. It is then scraped off every few days before it has an opportunity to become dirty or hard. From observations made at the time, I should estimate that healthy, mature trees will average 4 to 5 kilos of resin per year. I have seen as much as 22 kilos of *elemi* on one large tree, representing a two months' flow of the resin.

EXPERIMENTAL.

The fresh *elemi* resin was distilled *in vacuo,* the volatile oils being separated from water, shaken out with dilute alkalies, dried over calcium chloride, and redistilled *in vacuo,* only the terpene fraction being collected. The terpenes were then distilled at ordinary pressure. In Table I, the figures are given for series of these terpene oils representing samples of resin from individual trees, all being identified by Mr. Merrill from the botanical material as *C. luzonicum.* Under the column "Terpene," limonene is abbreviated as L; phellandrene, represented by P, stands for any terpene giving a crystalline nitrite of a melting point not over 121°. I will deal with the separate phellandrenes afterwards.

TABLE I.—*Manila elemis from Calaoag, Tayabas.*

No.	Terpene.	Boiling point.	Optical rotation, 10 cm. tube.	No.	Terpene.	Boiling point.	Optical rotation, 10 cc. tube.
		Degrees.	*Degrees.*			*Degrees.*	*Degrees.*
21	P	170 –173	+ 46	108	P	169 –172	+ 96.2
57	P	175 –178	+ 95	105	P	172 –174	+ 68.5
67	P	172 –175	+134.5	92	P	172 –174	— 35.5
55	P	172 –178	+126.0	111	P	169 –170	+ 70.5
69	P	172 –175	+125.5	98	P	171 –174	+ 30.3
56	P	172 –175	+ 82.2	97	P	172 –175	+ 94.8
92	P	170 –178	— 44.5	75	P	171 –174	+ 86.2
109	P	170 –173	+106.2	70	P	171 –174	+108.8
88	P	171 –174	+109.6	118	P	169 –173	+ 25.
106	P	171 –174	+119.6	72	P	172 –174.2	— 60.6
76	P	169 –172	+ 31.6	81	P	172 –175	+ 12.
78	P	169 –172	+ 31.0	91	P	172 –175	— 30.4
80	P	172 –174	— 50.5	120	P	171 –172.6	+ 99.7
86	P	173 –175	+ 83.7	84	P	172.5–174	+ 95.8
70	P	173 –175	— 24.4	95	P	171 –172.5	+117.5
73	P	169 –172	+ 42.5	74	P	169 –172	+ 24.5
117	P	169 –171	+ 46.5	63	P	170 –173	+ 84.0
82	P	171 –173	+109.0	71	P	170 –173	+ 95.5
110	P	170 –173	+ 37.9	112	P	172 –175	+ 89.9
90	L	175 –176.5	+ 96.0	113	P	168 –172	+ 88.
114	P	170 –173	— 33.3	101	P	176 –178	+ 91.8
122	P	171.5–174	+ 93.5	103	P	173 –175	+ 68.
83	P	171 –174	+116.0	102	P	176 –179	+ 85.2
116	P	172 –174	+ 7.5	85	P	169 –173	+ 48.9
77	P	169 –173	+ 65.5	119	P	172 –174	+ 54.4
99	P	169 –172	+ 78.7	115	P	173 –176	+ 48.9
100	P	172 –174	+ 16.0	46	P	175 –177	+ 45.3
13	P	171 –174	+ 66.	89	P	172 –175	+ 79.6
121	P	172 –175	+ 34.3	94	P	174 –176.5	+ 91.1
87	P	174 –176	+ 86.8	4	P	172 –174.5	+125.6
96	L	174 –176	+ 89.0	93	P	171 –174	+ 85.6

This table is striking because it shows the very great differences in boiling point and especially in optical rotation of the various terpene

oils. For purposes of further purification the terpenes were now united into five classes:

1. *Laboratory number B–3.*—Lower boiling phellandrenes. Seventeen samples numbered 109, 76, 78, 73, 117, 110, 77, 99, 108, 111, 118, 74, 63, 71, 113, 85, 59.

2. *Laboratory number B–4.*—High boiling phellandrenes. Five samples numbered 94, 46, 102, 87, 101.

3. *Laboratory number B–5.*—Middle boiling phellandrenes. Thirty samples numbered 88, 106, 86, 82, 122, 83, 116, 100, 13, 121, 105, 98, 97, 75, 70, 81, 120, 84, 95, 112, 103, 119, 115, 89, 4, 93, 61, 66, 58, 60.

4. *Laboratory number B–6.*—Phellandrenes with a negative optical rotation. Six samples numbered 80, 70, 114, 92, 72, 91.

5. *Laboratory number B–7.*—Limonenes numbered 90, 96.

Before discussing the above terpenes I desire to present nine specimens of very carefully purified terpenes from *elemi* resin obtained in Gumaca, Tayabas Province:

TABLE II.—*Manila elemis from Gumaca, Tayabas.*

No.	Terpene.	$N_D^{30°}$	Boiling point.	Specific gravity, $\frac{30°}{4°}$	$A_D^{30°}$
			Degrees.		
1	L	1.4674	175 –177	0.8360	116.8
2	Pβ	1.4658	[a]165 –169	0.8350	92.2
3	L	1.4673	175.5–178	0.8360	117.8
4	L	1.4672	175 –178	0.8359	111.8
5	Pα	1.4680	173 –175	0.8365	107.6
6	L	1.4670	[b]175 –178	0.8358	117.9
7	L	1.4670	175 –178	0.8363	117.6
8	Pβ	1.4660	166 –169	0.8355	90.7
9	L	1.4670	176 –177	0.8364	115.6

[a] Boiling point 63° to 64° at 15 millimeters.
[b] Boiling point 60° to 65° at 9 millimeters.

It will be noted that of this last series, six terpenes are limonene, two are β phellandrene, and one α phellandrene. It is interesting to note that almost all of the *elemi* collected by me in the neighborhood of Calaoag contained phellandrene, while that collected near Gumaca showed that six of the nine samples contained limonene. Clover [7] found a large per cent of the *elemis* which he examined to contain limonene. Of all the *elemis* from various sources which I have examined, over 90 per cent contained phellandrene.

Two phellandrenes α and β have been distinguished by chemists. These phellandrenes have been differentiated not only by their physical properties, but principally by their nitrites. Wallach [8] ascribes a melting point of 113° to 114° to the α modification of the nitrite of α phellandrene, the β modification of the nitrite of this terpene having a melting

[7] *Loc. cit.*
[8] *Ann. d. Chem.*, (Liebig) (1904), **336**, 9.

point of 105°. Schreiner [9] found 120° to 121° as the melting point of the *a* modification of *a* phellandrene nitrite. My work seems to show that if the phellandrene nitrite is crystallized from cold solvents it is very easy to isolate the body of the higher melting point. Wallach heated his solvents, which probably accounts for the lower melting point. The yield of phellandrene nitrite is very far from quantitative, hence it is not possible by use of the nitrites to determine whether a phellandrene is pure or contains other terpenes. Moreover, I was able to obtain a considerable yield of a phellandrene nitrite of a melting point of 121° from a terpene which from its physical properties and its behavior on oxidation, I believed to be practically pure β phellandrene. The experiments on the phellandrene nitrites follow:

(A) Supposed *a* phellandrene. The united specimens B–5 were three times distilled over sodium, *in vacuo*, and in the last distillation the terpene was collected in three equal fractions to test its unformity.

Boiling point at 12 mm. pressure.	Refractive index, $N_D^{30°}$	$A_D^{30°}$	Specific gravity, $\frac{30°}{4°}$
(1) 62 to 62.3	1.4680	92.2	0.8363
(2) 62.3 to 62.8	1.4680	91.2	0.8364
(3) 62.8 to 63.5	1.4683	91.0	0.8363

The whole, once redistilled at ordinary pressure, had a boiling point of 172° to 174°; specific gravity, $\frac{30°}{4°}=0.8363$ $N\frac{30°}{D}=1.4681$; $A\frac{30°}{D}=91°.4$. This terpene corresponds very well in its physical properties with the best published data for *a* phellandrene.

(1) 13.6 grams of this *a* phellandrene were added to 12 grams of sodium nitrite (Kahlbaum fused) dissolved in a small amount of water, and while the whole was immersed in a freezing mixture, with vigorous shaking, 12 grams of cold glacial acetic acid were added drop by drop. There were obtained 6 grams of crude phellandrene nitrite. This was purified by dissolving in cold chloroform and precipitating by ether. It was then recrystallized once from cold acetic ether, when 1.6 gram of a substance having a melting point of 120° to 121° was obtained.

(2) 13.6 grams *a* phellandrene obtained as in experiment (A) with 16 grams of sodium nitrite and 16 grams of glacial acetic acid, gave 8 grams of crude nitrite, which purified as above gave 2.2 grams of pure nitrite melting at 120°.

(B) Fractions 2 and 8 of the Gumaca terpenes were united and twice distilled over sodium, giving an oil of the following properties: Boiling point, 760 millimeters, 166° to 168°.2; specific gravity, $\frac{30°}{4°}=0.8354$; $N\frac{30°}{D}=1.4658$; $A\frac{30°}{D}=91°.2$. To judge from its boiling point, this terpene would be taken for β phellandrene and it seems hardly possible that it could contain any quantity of *a* phellandrene, yet it gives large quantities of the same nitrite as the *a* phellandrene.

(1) 13.6 grams β phellandrene, 12 grams of sodium nitrite, 12 grams of glacial acetic acid treated exactly as above gave 5 grams of crude nitrite which gave 1.2 grams of pure nitrite of a melting point of 121°.

[9] *Chem. Centralbl.* (1901), 2, 544.

In addition to the α and β phellandrene above noted, there would seem to be a higher boiling phellandrene in *elemi* resin, boiling point 175° to 178° at 760 millimeters; specific gravity, $\frac{30°}{4°}$ =0.8375; N $\frac{30°}{D}$ = 1.4685; A $\frac{30°}{D}$ 82.4. This phellandrene by the above treatment also gives the phellandrene nitrite melting at 121°. β phellandrene on oxidation with dilute potassium permanganate gives the aldehyde, phellandral, with an odor like cuminol, while this is not obtained with my α phellandrene. It is evident that much more extensive study is necessary to clear up the difficulties noted here and I will again take up this subject when I have obtained the two standard phellandrenes, the α from bitterfennel oil, *Fœniculum vulgare* Mill, and the β from waterfennel oil, *Phellandrium aquaticum* L. for comparative purposes. Semmler [10] oxidized phellandrenes with dilute potassium permanganate and the first products which he obtained he subsequently oxidized with lead superoxide, thus separating *quantitively* 1-isopropyl succinic acid from α phellandrene, and from β phellandrene α isopropyl glutaric acid, both being crystalline compounds easily identified. Semmler does not give the exact conditions under which he made these oxidations. I have oxidized my α and β phellandrenes with potassium permanganate under various conditions, but have never been able to obtain *quantitative* yields of these acids.[11] Unless quantitative yields can be obtained, it is evident that the method is not of much value in deciding the difficult question as to whether a sample of a phellandrene contains a small quantity of another phellandrene.

THE RESIDUE FROM THE DISTILLATION OF ELEMI.

From 12 to 18 per cent of terpenes are obtained by the distillation *of elemi in vacuo,* and from 12 to 15 per cent of a higher boiling oil, of which one of the constituents has recently been proved by Semmler [12] to be elemicin, (allyl-1-trimethoxy-3,4,5-benzol). The distillation residue, usually amounting to about 70 per cent of the *elemi,* is a light brown, transparent, solid resin, with a brillant fracture. This *elemi* residue is completely and easily soluble in the cold in the following solvents: Alcohol; ether; benzol; petroleum ether; ligroin; xylol; choloroform; amyl acetate; acetone; methyl alcohol; carbon tetrachloride; ethyl acetate; turpentine; amyl alcohol, and glacial acetic acid.

[10] *Ber. d. deutschen chem. Ges.* (1903), **36**, 1749.

[11] Kondakow (*Journ. f. prakt. Chem.* (1908), n. s. **78**, 42) has recently proved that, contrary to the long accepted view, the phellandrene from *Phellandrium aquaticum* is not an individual terpene, but contains over 20 per cent of pinene. He announces a thorough investigation of the whole phellandrene chemistry. Kondakow's work throws grave doubt on the quantitative yields claimed by Semmler for the oxidation of these terpenes with potassium permanganate.

[12] *Ber. d. deutschen chem. Ges.* (1908), **41**, 1768, 1918, 2183.

Solutions in these solvents leave a brillant varnish coat which, however, dries quite slowly. The resin dissolves only very slowly in cold kerosene and in chloral hydrate, but quite easily on warming with these solvents.

The use of *elemi* residues with turpentine and linseed oil has not given us very satisfactory varnishes, for even with excessive quantities of driers, the varnish coat remains somewhat sticky for three or four days. This *elemi* residue, however, mixed with varying proportions of Manila copal, melted with boiled linseed oil, and properly thinned with turpentine has given us most excellent varnishes, which give a hard, brillant, and elastic coating on wood. The use of the *elemi* resin residue for varnishes seems not only to give a paler and more brilliant varnish than copal alone, but renders the melting of the copal much easier. I believe this *elemi* resin distillation residue has a future as a varnish gum. This entire question will be taken up by George F. Richmond, Bureau of Science, who is now studying Manila copals.

In this connection I desire to note a few further experiments on the distillation of Manila *elemi*. The resin as it comes into the market is often mixed with bark, dirt, and other impurities. Before shipment to Europe these impurities are usually picked out by hand as far as possible. Solution of the resin in alcohol, filtering, and distilling off the alcohol even *in vacuo*, leaves a dark colored resin, which in appearance is not at all like elemi. The best method of purifying *elemi* resin is by solution in benzol, filtering, and distillation of the benzol, when a white resin of the same leafy appearance as *elemi* is obtained.

Six and five-tenths kilos of commercial *elemi* were distilled in the usual manner *in vacuo*, and the volatile oil redistilled at ordinary pressure. The following fractions, each of about 135 cubic centimeters, were obtained:

	Boiling point, degrees (760 mm.).	Rotation in a 10 cm. tube (degrees).
(1)	168–174	99.1
(2)	174–177	95.5
(3)	177–179	95.0
(4)	179–181	92.0
(5)	181–183	90.0
(6)	183–190	83.0
(7)	190–210	63.0

These fractions were now washed with dilute alkalies, dried and refractioned with the following results:

No.	Quantity.	Boiling point, degrees (760 mm.).	$A\frac{30°}{D}$	10 cm. tube.	$N\frac{30°}{D}$	Specific gravity, $\frac{30°}{4°}$
	cc.					
1	100	169–170	118.8	99.0	1.4680	0.8345
2	440	170–173	113.9	95.0	1.4680	0.8357
3	170	173–175	103.4	86.5	1.4684	0.8363
4	160	175–180	88.1	74.0	1.4697	0.8396
5	45	180–190	76.8	65.0	1.4712	0.8463

The total yield of terpene oil was 14 per cent. The greater part of these terpenes consisted of phellandrenes, although in the higher boiling fractions, dipentene (present only a very small amount) could be detected by the formation of dipentene tetrabromide melting at 124°. It is evident from the two above-mentioned distillations that there is very little decomposition caused in phellandrenes by distilling them at ordinary pressure. To test more thoroughly the effect of such distillations, 2 kilos of the same lot of *elemi* resin were worked up just as in the above experiments, save that all distillations were made *in vacuo*. After the second distillation of the terpene oil, the following fractions were obtained, each number representing about 55 cubic centimeters of oil in a 10-centimeter tube.

	Boiling point, degrees (6 mm.).	Optical rotation, 10 cm. tube, N $\frac{30°}{D}$ (degrees).
(1)	51 –51	101
(2)	51 –52	101
(3)	52 –52.5	98
(4)	52.5–54	93
(5)	54 –57	83
(6)	57 –60	83

This experiment shows that there has been a slight lowering of the optical activity of the phellandrene due to distillation at ordinary pressure. This has been my experience in other experiments. In repeatedly distilling 300 grams of *α* phellandrene, I have noted, after each distillation, that the optical rotation is lowered by 0°.5 to 1°.0. None of the other constants of the terpene are affected, and phellandrenes are not as sensitive to heat as would be judged from the statements on this subject in the literature. Sunlight affects the optical activity of phellandrenes much more markedly than heat, as is shown by the following:

Sample 55, Calaoag resins, *α* phellandrene. Rotation in a 10-centimeter tube, 134°.5. After two hours in the sunlight, 132°.0. After eight hours more of sunlight, 124°.7.

Sample 69, *α* phellandrene. Rotation in a 10 centimeter tube, 125°.5; after one week's exposure to the sun 101°.5.

Sample 99, *β* phellandrene. Optical rotation in a 10-centimeter tube, 78°.7. After one week's exposure to the sunlight, 32°.1. This phellandrene had then become markedly thicker and more viscous. Pesci [13] obtained a glassy mass $(C_{16}H_{16})x$, melting at 86°, by heating *β* phellandrene for twenty hours in a sealed tube from 140° to 150°. The *β* phellandrene from *elemi* is not nearly as sensitive to heat as this phellandrene from waterfennel oil, which Pesci used.

Sample 90, *α* limonene. Optical rotation in a 10-centimeter tube, 96°.0. After one week's exposure to the sunlight, 94°.9. Sunlight, therefore, has very little effect on limonene.

[13] *Gazz. chim. ital.* (1886), **16**, 225; *Ber. d. deutschen chem. Ges.* (1886), Ref. **19**, 874.

The following experiments probably throw a little light on the whole question of the sensitiveness of various terpenes to heat, light, etc.

Two sealed tubes were heated in a bomb furnace from 270° to 300°, one containing limonene from *elemi*, the other limonene from orange-peel oil. After five hours the limonene from *elemi* had decreased in its optical rotation by only 1°.3, while that from orange oil had decreased 14°.7. Wallach[14] states that by several hours' heating at 250° to 270°, hesperidene (*d*–limonene from orange-peel oil) is changed to dipentene. Clover[15] found limonene from *elemi* to be little changed by heat. The above experiments would seem to show that both statements are correct, and it seems probable to me that the change in the limonene from orange-peel oil is due to a small amount of a catalyzing impurity in this substance. I am strengthened in this supposition by the fact that whereas limonene is relatively stable in light and air, orange-peel oil containing over 90 per cent of limonene is exceedingly sensitive to light and air, and very readily change into a resinous mass. Some experiments which I made on Philippine oranges point in the same direction. The peel of the native orange contains a very large quantity of oil, but this is so unstable that in the course of two minutes a rather thick layer of it will be completely converted into a solid resin. I finally succeeded in obtaining a small quantity of this orange-peel oil by squeezing it onto sponges soaked in sodium carbonate solution, and over 90 per cent of the oil proved to be a *d*–limonene boiling at 174° to 176°, giving a tetrabromide melting at 104° and limonene nitrolbenzylamine melting at 93°. I consider, therefore, that many cases of observed changes in terpenes on heating may not represent intrinsic properties of the terpene itself, but may be due to small traces of impurity, for in layers of similar thickness, Philippine orange-peel oil, consisting of 90 per cent of limonene, changes to a resin several hundred times as fast as limonene itself.

DESTRUCTIVE DISTILLATION OF THE "ELEMI" RESIN.

The residue of *elemi* from which the volatile oils had been distilled *in vacuo* was used in this experiment, as there is very little destruction at the temperature at which the terpenes distill at ordinary pressure, and I did not wish to contaminate the resin oil with the terpene.

One kilo of this residue was distilled in a 2-liter Jena flask. It melts quietly with very little darkening and no foaming, evolution of gas, or other signs of decomposition. As the temperature is increased, considerable cracking and evolution of water soon takes place and the whole mass becomes very dark, the oil beginning to distill at a vapor temperature of 200°. The whole distillation is very quiet with no foaming or frothing and very little evolution of gas. The oil at first is green, then an intense, fluorescent blue and toward the close of the distillation almost white. The total distilled was 670 cubic centimeters of which 40 were the aqueous layer. Three hundred and ten grams of black tar were left in the distilling flask. The oil, shaken out with dilute alkalies, gave 18 grams of acids, while after saponification with alcoholic potash a further 7 grams

[14] *Ann. d. Chem.*, (Liebig), (1885), **227**, 289.
[15] *Loc. cit.*

of acids were obtained. The neutral oils distilled *in vacuo* gave fractions at 10 millimeters of about 90 grams each, as follows:

No.	Boiling point. 10 m. m.	$N\frac{30°}{D}$	Specific gravity, $\frac{30°}{4°}$	$A\frac{30°}{D}$
	Degrees.			*Degrees.*
1	80–89	1.4650	0.842	18.1
2	89–130	1.4830	0.871	12.2
3	130–145	1.4970	0.916	----------
4	145–155	1.5030	0.932	----------
5	155–158	1.5100	0.952	----------
6	160–180	1.5270	0.968	----------
7	Residue a thick, viscous, tarry oil.			

There were no indications of any separable, individual products, and nitration and oxidation of these fractions under various conditions gave no promise of obtaining individual compounds. This oil obtained by the destructive distillation of *elemi* is evidently a resin oil of the same general character and useful for the same purposes as other resin oils.

I have examined two specimens of *elemi* resin, one being from Culion and the other from the Island of Mindanao, which were unusual in that the terpene was almost entirely pinene, a solid hydrochloride melting at 125° being obtained from each specimen. A few *elemis* from Mindoro gave the following results:

(1) Two kilos resin gave 240 cubic centimeters terpenes. Boiling point, 172° to 174°; specific gravity, $\frac{30°}{4°}=0.8344$; $N\frac{30°}{D}=1.4680$; $A\frac{30°}{D}=115.5$. The terpene proves to be phellandrene, giving a crystalline nitrite melting at 121°. Probably this is *α* phellandrene.

(2) One kilo resin, which has become somewhat hard, gave 95 cubic centimeters terpene. Boiling point, 175° to 177° at 760 millimeters; specific gravity, $\frac{30°}{4°}=0.8383$; $N\frac{20°}{D}=1.4687$; $A\frac{30°}{D}=111.0$. This gave a good yield of tetrabromide melting at 105°. Therefore, the terpene is *α* limonene.

(3) Five hundred grams resin gave 60 cubic centimeters terpenes. Boiling point, 177° to 180° at 760 millimeters; specific gravity = 0.8383; $N\frac{30°}{D}=1.4687$; $A\frac{30°}{D}=7.3$; tetrabromide melts at 124°. This terpene is principally dipentene.

(4) Five hundred and twenty grams resin gave 74 cubic centimeters oil. Boiling point, 172° to 173°.5 at 760 millimeters; specific gravity, $\frac{30°}{4°}=0.8341$; $N\frac{30°}{D}=1.4678$; $A\frac{30°}{D}=114.8$. Abundant precipitate of phellandrene nitrite melting after purification at 120°. Probably *α* phellandrene.

(5) One and one-tenth kilos resin gave 140 cubic centimeters terpene. Boiling

point, 166° to 168° at 760 millimeters; specific gravity, $\frac{30°}{4°}=0.8354$; $N\frac{30°}{D}=1.4658$; $A\frac{30°}{D}=91.5$. This terpene oil gave an abundant precipitate of phellandrene nitrite and was considered to be β phellandrene.

LIMONENE.

The various samples of terpenes from *elemi* which were considered to be pure *d*–limonene were united and after three distillations over sodium gave an oil boiling between 176° to 177°.4 (thermometer wholly in vapor); with a specific gravity, $\frac{30°}{4°}=0.8356$; $N\frac{30°}{D}=1.4670$; $A\frac{30°}{D}=115.7$. This oil yielded limonene tetrabromide melting at 104°. Repeated distillations over sodium always gave the same range in the boiling point and no change in the optical activity, and therefore, I consider this to be a very pure sample of limonene.

I have obtained more satisfactory results in preparing the hydrochlorides and hydrobromides of terpenes, by using petroleum ether to dilute the terpene, instead of carbon bisulphide as recommended by Wallach. Petroleum ether has the advantage of permitting the terpene and the solvent to be distilled over sodium directly before the dry hydrogen halide is run into the mixture and absolute certainty that everything is anhydrous is assured. Limonene hydrochloride prepared with petroleum ether as a solvent is a much purer product than when carbon bisulphide or any other solvents are used; the body made in this way boils within 2° or 3° on the first distillation *in vacuo*, while with carbon bisulphide a range of 10° to 15° is common and several fractionations are necessary to obtain a pure product.

I have also been able to prepare pure limonene hydrobromide and phellandrene hydrochloride by this method; the properties of these bodies are not recorded in the literature.[16]

In a previous article[17] in this series, I have shown that limonene hydrochloride reacts with magnesium according to the Grignard reaction, the product of the decomposition of the hydro-limonene magnesium chloride with water being a dihydroterpene $C_{10}H_{18}$. This dihydroterpene instead of the expected carbinol was also obtained with benzaldehyde, the benzaldehyde behaving as if it contained a hydroxyl group. A continuation of this line of research has shown that while terpene halides in general easily react with magnesium in the presence of ether, the addition products so formed do not readily enter into reaction with other

[16] A uniform, easily controlled stream of dry hydrogen bromide may be obtained by the following method: Red phosphorus is covered with a layer of completely saturated, aqueous hydrobromic acid, and a mixture of 3 parts bromine and 1 part saturated hydrobromic acid is dropped slowly into this mixture. The gas is evolved quietly and regularly and after passing two wash bottles containing red phosphorus, suspended in saturated hydrobromic acid, is dried by means of a long tube of granulated calcium chloride. There is practically no contamination with hydrochloric acid by this method, although calcium bromide would be better for drying purposes.

[17] *This Journal, Sec. A.* (1908), **3**, 49.

substances, as would be expected from bodies of this nature formed according to the reaction of Grignard. I will record but a few of the experiments performed to show the type of reactions.

LIMONENE HYDROCHLORIDE.

(1) Limonene from *elemi*, distilled over sodium with an equal volume of petroleum ether, was saturated with dry hydrochloric acid gas; limonene hydrochloride with the following properties was obtained on distilling this product *in vacuo:*

Boiling point at 12 millimeters' pressure, 95° to 97°, specific gravity, $\frac{30°}{4°}$ = 0.9616; N $\frac{30°}{D}$ =1.4758; A $\frac{30°}{D}$ =80°.1; yield, 90 per cent.

	Found (per cent).	Calculated (per cent).
Cl	20.2	20.3

Fifty grams of this limonene hydrochloride, 10 grams of magnesium, and 100 cubic centimeters of absolute ether were allowed to react in an atmosphere of dry hydrogen. When the reaction was over, 45 grams (calculated 43 grams of ortho-formic ester) were added.[18] The resulting reaction was not violent and, therefore, the mixture was heated for two hours on a steam bath, the greater part of the ether escaping through the reflux condenser. The yellowish, solid reaction product was during the next morning treated in the usual manner by placing it upon crushed ice and adding dilute, cold sulphuric acid. There were thus obtained 48 grams of an oil (calculated 85 grams). This oil consisted principally of the dihydroterpene $C_{10}H_{18}$ boiling at 171° to 173°; N $\frac{30°}{D}$=1.4610. The ortho-formic ester had apparently disappeared in the aqueous solution, as alcohol and formic acid were both easily detected therein.

(2) Limonene hydrochloride 60 grams, absolute ether 150 cubic centimeters, magnesium 10 grams. After the reaction was over, 60 grams of ortho-formic ester were added with very vigorous stirring. The apparatus was arranged to catch any gas which might be evolved during the reaction, but none was obtained. After heating for two hours on a steam bath, the reaction mass was separated into ether soluble and ether insoluble portions, and each portion was decomposed separately with ice and dilute sulphuric acid.

Portion soluble in ether.

Alcohol, 23.1 grams.
Formic acid, 8 grams.
Oil, 45 grams, which consisted of 7 grams "Vorlauf," 34 grams of $C_{10}H_{18}$, and 4 grams of a high boiling oil. The "Vorlauf" contained considerable quantities of ethyl formate and the high boiling oil gave no reaction with phenylhydrazine, even after boiling with dilute acids and was probably principally a diterpene.

Portion insoluble in ether.

Alcohol, 12.5 grams.
Formic acid, 7.5 grams.
High boiling oil, 5 grams. This latter oil boils at 150° to 220° at 10 millimeters, leaving a tarry residue of 2.3 grams. The 2.5 grams high boiling oil, distilled once gave no reaction with phenylhydrazine, and dilute boiling acids had no effect on it.

[18] Kahlbaum fractioned several times over small amounts of sodium with which it reacts only slightly; boiling point, 144° to 146°; N $\frac{30°}{D}$=1.3935.

These experiments show that a reaction, which is very different from the normal one between ortho-formic ester and organo-magnesium halides, had taken place. It is to be noted that the great tendency in the terpene series during reactions of this nature, is to produce the reduced terpenes. To exclude any possibility that these reduced terpenes might result from the action of the sulphuric acid used in decomposing the reaction mass, or any excess of magnesium, I attempted to reduce limonene, α phellandrene, and β phellandrene with magnesium and dilute sulphuric acid. The results were absolutely negative. The refractive index of the terpene was in each case the same before as after the attempt at reduction.

Oxygen reacts with hydrolimonene magnesium chloride to give terpineol as is shown by the following result:

One hundred and ten grams of limonene hydrochloride, 20 grams of magnesium, 300 cubic centimeters of absolute ether. After the reaction according to Grignard was completed, I ran a copious stream of dry oxygen into the apparatus during eight hours. There was a considerable evolution of heat and reddening of the mass. The products of the reaction were decomposed by means of a cold solution of ammonium chloride, and the resulting oils were fractional *in vacuo*. Nine grams of terpineol, boiling between 98° and 102° at 9 millimeters' pressure were thus obtained; specific gravity, $\frac{30°}{4°}=0.930$; $N\frac{30°}{D}=1.4805$; $A\frac{30°}{D}=15°.2$. The phenyl urethane derivative was prepared in a solution of petroleum ether and when once recrystallized melted at 112° to 113°. The lower boiling fractions of this oil (78 grams), boiling between 172° and 175° at ordinary pressure, still had some terpeneol odor. Specific gravity, $\frac{30°}{4°}=0.8250$; $N\frac{30°}{D}=1.4617$. Therefore, this oil probably consisted largely of the dihydroterpene $C_{10}H_{18}$.

LIMONENE HYDROBROMIDE.

Seventy-five grams of dry limonene, dissolved in an equal volume of dry petroleum ether, were saturated with dry hydrogen bromide. Distillation *in vacuo* gave 45 grams of limonene hydrobromide, boiling between 108° and 112° at 12 millimeters' pressure; specific gravity, $\frac{30°}{4°}=1.1209$; $N\frac{30°}{D}=1.5006$.

	Found (per cent).	Calculated (per cent).
Br.	35.8	36.4

Limonene hydrobromide was allowed to react according to the method of Grignard with 8 grams of magnesium. The reaction is more vigorous than with the corresponding hydrochloride. A test-tube experiment showed that the hydrolimonene magnesium bromide did not react with chlorocarbonic ester. Twenty grams of benzaldehyde were then added to the hydrolimonene magnesium bromide. The reaction was very vigorous, a yellow solid separating just as in the similar reaction with the hydrochloride. The products obtained were principally benzaldehyde and dihydrolimonene. The reaction with benzaldehyde is, therefore, exactly the same as when limonene hydrochloride is used.

LIMONENE HYDROBROMIDE AND ACETALDEHYDE.

Limonene hydrobromide with the following properties, boiling point at 10 millimeters, 106° to 109°, specific gravity, $\frac{30°}{4°}=1.1211$; $N\frac{30°}{D}=1.5012$; bromine found, 36.1; calculated, 36.4 per cent. Fifty grams of this hydrobromide were subjected to the Grignard reaction with 10 grams of magnesium. After the reaction was complete, 15 grams of acetaldehyde were slowly distilled into the mixture. There is marked heating and a yellowish, sticky solid separates. From this solid, using the usual method of treatment, there were obtained 27.0 grams of $C_{10}H_{18}$ (calculated, 31.3 grams), boiling point, 173° to 175° at 760 millimeters, specific gravity, $\frac{30°}{4°}=0.8256$; $N\frac{30°}{D}=1.4583$. The residual oil, 3.5 grams, contained a trace of halogen, had no hydroxyl groups, and was probably a diterpene. Acetaldehyde, therefore, reacts on hydrolimonene magnesium bromide just as does benzaldehyde.

It is very interesting to note that hydrolimonene magnesium bromide is, when first formed, a liquid insoluble in ether. After lying under the ether for a few days it changes into a crystalline solid insoluble in ether.

LIMONENE DIHYDROBROMIDE AND BENZALDEHYDE.

One hundred grams of limonene from orange-peel were mixed with an equal volume of absolute ether and saturated with dry hydrogen bromide, 150 grams of crystalline dihydrobromide melting at 64° (from ether) resulted.[19] A mixture of 150 grams of limonene dihydrobromide and 150 grams of benzaldehyde was slowly added to 35 grams magnesium, which had been rendered active, in 400 cubic centimeters of ether. A fairly vigorous reaction took place. The reaction mixture was decomposed with ice and dilute sulphuric acid, the oils were poured into petroleum ether, and 14 grams of a crystalline solid separated. This was recrystallized several times from benzol. It is moderately soluble in hot benzol, insoluble in the cold, almost insoluble, hot or cold, in ether, petroleum ether, ligroin, acetic ester, methyl or ethyl alcohol, acetone, or carbon bisulphide. The melting point is not sharp. At 195° the compound begins to darken and at about 212° it melts with marked decomposition. The compound used in the following analysis had been recrystallized 15 times from benzol and consisted of beautiful, white crystals which under the microscope seemed to be homogenous.

0.2000 gram substance gave 0.2181 gram AgBr.

0.2000 gram substance gave 0.2180 gram AgBr.

0.2340 gram substance gave 0.4365 gram CO_2 and 0.0590 gram H_2O.

0.2730 gram substance gave 0.5100 gram CO_2 and 0.0700 gram H_2O.

0.5 gram dissolved in 27 grams benzol raised the boiling point 0°.065.

	Calculated for $C_{30}H_{60}Br_4$ (per cent).	Calculated $C_{29}H_{50}Br_4$ (per cent).	Found (per cent).	Found (per cent).
C	51.40	50.58	50.93	50.90
H	2.85	2.90	2.80	2.84
Br	45.70	46.49	46.40	46.40
Molecular weight	700.00	690.00	745.00	.....

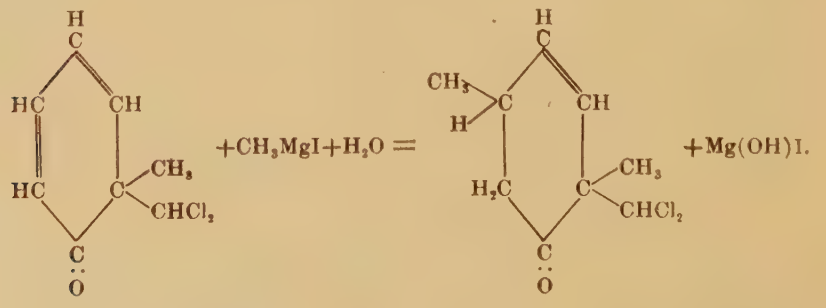
[19] The dihydrohalide always results no matter how thoroughly dried the solvent has been, when hydrogen halides are run, to saturation, into limonene dissolved in ether, while with petroleum ether, only the mono compound is obtained.

The other principal products of the reaction are benzaldehyde and tetrahydrolimonene $C_{10}H_{20}$.

Another bromine determination was made on some of the compound, the analysis of which is given above, crystalized eight times from benzol. 0.2000 gram substance gave 0.221 gram AgBr. Bromine found, 46.8 per cent.

This would seem to show that I was dealing with a pure compound. The reaction which has taken place is so entirely different from the normal course of the Grignard reaction that even speculation as to the nature of this crystalline compound is out of the question. The percentage of hydrogen is so low that it would seem as if limonene had taken no part in the reaction. It is still more difficult to see how bromine could unite with a benzaldehyde derivative in the presence of activated magnesium. The extensive literature of the Grignard reaction shows that, while this method has a very wide applicability, there nevertheless are very many cases in which the reaction proceeds in an abnormal direction, especially when other than the halides of the first members of any given series are used.

Thus, isoamyl magnesium bromide with benzophenone does not give the diphenyl isoamyl carbinol which would be expected, or the dehydrated hydrocarbon derived from it, but benzhydrol and benzhydrol ether.[20] Similarly, benzyl alcohol is one of the reaction products in the action of ethyl magnesium iodide on benzaldehyde.[21] J. Schmidlin and H. Hodgson,[22] in speaking of the action of various reagents on β triphenyl magnesiumchlormethane $(C_6H_5)_3C.MgCl$, say "Es scheinen somit diese Reagenzien, Aceton, Acetaldehyd, Acetylchlorid, so zu wirken, dass sie die MgCl-Gruppe abreissen, ohne sich mit dem verbleibenden Triphenylmethylrest zu verbinden." Auwers and Hessenland[23] found that it was impossible to obtain a normal reaction with alkyl magnesium halides and 2-methyl-2-dichlormethyl 1-keto-dihydrobenzol. With methyl magnesium iodide they observed the following reaction:



[20] Schorigin, *Ber. d. deutschen chem. Ges.* (1908), **41**, 2715. Konowalow, *Journ. Russ. phys. chem. Ges.* (1902), **34**, 26; (1908), **38**, 447.

[21] Schorigin, *Ber. d. deutschen chem. Ges.* (1908), **41**, 2721.

[22] *Ibid.*, 431.

[23] *Ibid.*, 1790.

There was no action on the carbonyl group. It is well-known that very many reactions carried out according to the Grignard method give yields which are not by any means quantitative. The secondary products which will throw so much light on the mechanism of this reaction have, as a general rule, been utterly neglected. It is exceedingly probable that these reactions take place in many different directions, depending upon the conditions and upon the reacting masses, as is shown by my work in the terpene series.

PHELLANDRENE.

PHELLANDRENE HYDROCHLORIDE.

The united terpenes of series Calaoag B–3 were distilled over sodium *in vacuo;* boiling point, 64°.5 to 65° at 15 millimeters (62° to 62°.5 at 10 millimeters); specific gravity, $\frac{30°}{4°}=0.8349$; $N\frac{30°}{D}=1.4657$; $A\frac{30°}{D}=77°.8$. An equal volume of dry ligroin was added and the terpene was then saturated with dry hydrogen chloride. After removing the liquid, the residual oil was distilled at 1 millimeter pressure; boiling point, 80° to 83°; specific gravity, $\frac{30°}{4°}=0.960$; $N\frac{30°}{D}=1.4770$; chlorine found, 20.2 per cent; chlorine calculated, 20.3 per cent.

The odor of this hydrochloride is much like that of the corresponding limonene derivative. Phellandrene hydrochloride did not react completely with magnesium in the presence of ether; therefore, phellandrene hydrobromide was prepared. This compound can not be distilled *in vacuo* without decomposition and in fact it slowly decomposes with evolution of hydrobromic acid even at the ordinary temperature. Phellandrene hydrochloride begins to split off hydrochloric acid at about 85°, and must be distilled below that temperature.

PHELLANDRENE HYDROBROMIDE.

α phellandrene, boiling point at 9 millimeters 62° to 63°; specific gravity, $\frac{30°}{4°}=0.8364$; $N\frac{30°}{D}=1.4673$, was mixed with an equal volume of dry petroleum ether and saturated with dry hydrogen bromide. After removing the petroleum ether the crude hydrobromide had the following properties: Specific gravity, $\frac{30°}{4°}=1.1302$; $N\frac{30°}{D}=1.5018$; bromine found, 37.6 per cent; calculated, 36.8 per cent. 70 grams of this hydrobromide were subjected to the Grignard reaction with 10 grams of magnesium and 200 cubic centimeters of absolute ether, and after the reaction was complete, 40 grams of benzaldehyde were added. A yellow-white solid separated. The reaction mixture was separated into ether soluble and ether insoluble substances, and each portion was separately decomposed with ice and dilute sulphuric acid.

Portion soluble in ether.	*Portion insoluble in ether.*
0.3 gram magnesium, 29 grams benzaldehyde phenylhydrazone corresponding to 15.6 grams benzaldehyde; 34 grams $C_{10}H_{18}$, boiling point, 169° to 173°; specific gravity, 0.8220; $N\frac{30°}{D}=$ 1.4600. 11 grams higher boiling oil from which there were separated by means of ligroin 0.8 gram of a halogen-free, crystalline solid. After purification by several crystallizations from petroleum ether, it melted at 137° and proved to be benzoïn, by melting it with that substance.	2.5 grams benzoïn, melting point 136° to 137°, 38 grams phenylhydrazone of benzaldehyde corresponding to 20.5 grams benzaldehyde.

The reaction between hydrophellandrene magnesium bromide and benzaldehyde thus corresponds exactly to the similar limonene reaction already studied in a previous paper.[24] Several additional experiments were performed with phellandrene hydrobromide and benzaldehyde under varying conditions, but in every case dihydrophellandrene and benzaldehyde were the principal products of the reaction.[25]

PHELLANDRENE DIHYDROCHLORIDE.

The dihydrochloride of phellandrene was also prepared. It does not crystallize and is quite unstable, evolving hydrogen chloride at the ordinary temperature. It does not react well with magnesium according to the Grignard reaction.

THE FORMATION OF DIPENTENE.

I have succeeded in converting α phellandrene into dipentene.

The chloride of α phellandrene was heated for six hours on a reflux condenser with an excess of alcoholic potash, and the product shaken out well with water, dried with calcium chloride and distilled. The greater part of the terpene now boiled at 178° to 180° and had no optical activity. This terpene was dissolved in an equal volume of amyl alcohol and two volumes of ether, together with 0.7 volume of bromine, were added slowly on a freezing mixture. After several weeks in the ice box, a large yield of crystalline dipentene tetrabromide, which after crystallization from acetic ether melted at 124°, was obtained. The original α phellandrene treated in the same manner and then inoculated with a crystal of the tetrabromide showed the presence of no dipentene.

[24] *Loc. cit.*

[25] The majority of terpenes when treated with iodine are oxidized to *p* cymol. Specimens of α and of β phellandrene were allowed to stand for two months with an excess of iodine. They were then shaken out with alkalies, dried and distilled and each gave a large yield of *p* cymol, with the following properties: Boiling point, 174° to 176°; specific gravity, $\frac{30°}{4°}=0.8489$; $N\frac{30°}{D}=1.4970$.

BROMINE ADDITION PRODUCT OF PHELLANDRENE.

One hundred and six grams of bromine were slowly added to 80 grams of α phellandrene dissolved in 100 grams glacial acetic acid. The bromination proceeded quite smoothly, without any evolution of hydrobromic acid. When treated in this manner one molecule of α phellandrene adds only two atoms of bromine. This dibromophellandrene reacts very satisfactorily according to the method of Grignard, and by decomposing the reaction products with water, 25 grams of a dihydroterpene $C_{10}H_{18}$ were obtained boiling between 170° and 172°; specific gravity, $\frac{30°}{4°}=0.8231$; $N\frac{30°}{D}=1.4590$; and 13 grams of terpene polymerization products still containing a small amount of bromine.

LEMON GRASS OIL.

Andropogon citratus DC. is not cultivated on a large scale in the Philippines, although it is found growing as a garden herb and also in the wild state in all parts of the Islands, being quite abundant in the highlands of the Province of Benguet. No commercial distillation of the oil is carried on at the present time. The first mention of lemon grass from the Philippines dates from 1635, when Juan Eusebeus Nuremberg, a Spanish Jesuit, describes it quite unmistakably under the name of *"tanglat."* This is still the Tagalog name for the plant. The correct spelling is *"tañglad."* Another name is *salai,* and in the Visayas this grass is termed *balyoco,* while the Spanish name is *Paja de Meca.* Many Filipinos have small patches of the grass. It is cooked with stale fish to improve the taste and is used as a flavor in wines and various sauces and spices; it is also used medicinally, being applied to the forehead and face as a cure for headache, and an infusion is held in the mouth to alleviate the suffering of toothache. It is also used for baths and fomentations, particularly in female complaints. The writings of the older botanists show that these uses date back to the first mention of the plant from the Malay regions. A perusal of the extensive literature on lemon grass oil leaves considerable doubt as to whether the cultivation of the grass for oil distillation in the Philippines should be recommended. The market for lemon grass oil must always remain quite limited, and it has been stated that the oil from one of the species of Australian eucalyptus, *Backhousia citriodora* F. Muell. would soon drive out that from lemon grass as a source of citral. The oil from this Australian plant has a citral content which is from 10 to 20 per cent higher than that from lemon grass, still it seems probable, in view of the great differences in the price of labor in Australia and in tropical countries, that lemon grass will be able to hold its own as the source of the world's supply of citral. The price of lemon grass oil has been very low during the past two years and the further cultivation of it has been strongly discouraged by European essential-oil houses. Still the plant has some

advantages. It gives quick results, the first returns coming in about six months after planting, and on the virgin soils of the Philippines it grows luxuriantly without any cultivation or care. I am strongly inclined to recommend it as a catch crop to help pay plantation expenses until the slower growing staple crops are ready to be harvested.

It is almost impossible to obtain from the literature any idea as to the yield of oil per hectare. On this point I note the following statements. About 300 kilos lemon grass yield 1 kilo oil.[26] Under normal conditions an annual yield of 8,000 ounces oil per acre can be reckoned upon. The grass is cut twice a year.[27] 496 pounds fresh lemon grass yield 1 pound of crude oil (0.2 per cent). The annul yield per acre amounts to about 20 pounds of crude oil. The grass is cut three to four times per year.[28] The average yield per acre is 49 quarts of lemon grass oil.[29] One acre yields 100 quarts of oil (lemon grass oil).[30] From thoroughly dried leaves, which had lost 70 per cent of their original weight, 8 to 8.5 per cent of oil was obtained, while leaves distilled immediately after the harvest yielded in the rainy season 2 per cent and in the dry season 5.5 per cent oil.[31]

Perhaps, considering the many possible variations of soil, climatic conditions, etc., these wide differences of oil yield are not remarkable. It must also be remembered that there are many varieties of lemon grass. We have never been able to obtain Philippine lemon grass in flower and hence can give no data as to the variety or varieties growing wild on these Islands. In fact, no accurate botanical determinations of the grass have been made for the same reason and it is assigned to *Andropogon citratus* DC. solely from the character of the oil obtained from the grass.[32] We obtained one shipment from Benguet which we worked up directly, but, in view of all these facts it was considered necessary to plant experimental plots of lemon grass. One lot was grown from grass obtained in Manila, at the Singalong experiment station of the Bureau of Agriculture on ground which has at various times had abundant applications of fertilizers, and another from Lamao plants was grown at the Government agricultural farm at Lamao, Bataan, on unfertilized virgin soil. The results obtained from these plots of grass were as follows:

Lamao.—Planted February 14, 1908. First cutting July 29, 1908. Obtained 432 kilos grass, from 57 square meters of ground, distilled two days after cutting, the yield was 900 grams of oil (0.2 per cent) of the following properties: Specific gravity, $\frac{30°}{4°}=0.894$; $N\frac{30°}{D}=1.4857$; $A\frac{30°}{D}=+8.1$; citral=79 per cent; Shimmel's test passes the oil.

[26] *Journ. agr. trop.* (1905), **5**, 42.

[27] *Kew Bull.* (1906), No. 8,364.

[28] *Bull. Imp. Inst.*, London (1907), **5**, 300.

[29] *Trop. Agr.* (1904), **24**, 35.

[30] *Ibid.*, (1905), **25**, 672.

[31] *Bull. Chambre Agr. Cochinchine* (1908), **11**, 218.

[32] The very confused botany of the oil-producing grasses has only recently been cleared up by the excellent monograph of Otto Stapf. *Kew Bull.* (1906), No. 8, 297.

The grass from the same plot was again cut about four months later (November 23, 1908) and yielded 230 kilos, giving on distillation 467 grams of oil of the following properties: Specific gravity, $\frac{30°}{4°}=0.8841$; $N\frac{30°}{D}=1.4765$; $A\frac{30°}{D}=+2.1$; citral=77 per cent; Schimmel's test passes the oil.

Singalong station plot.—134 square meters planted on November 6, 1907, and cut July 27, 1908, gave 545 kilos grass which distilled immediately gave 1,145 grams (0.21 per cent) oil of the following properties: Specific gravity, $\frac{30°}{4°}=0.891$; $N\frac{30°}{D}=1.4812$; $A\frac{30°}{D}=+7.76$; citral=78 per cent; Schimmel's test passes the oil.

All of these oils were distilled with steam in this laboratory and were of a very light yellow color when first distilled. It was noted that on standing in colorless, glass-stoppered bottles in the light, they darken to a brown color in a few months.

Three hundred and thirty-five grams of the Singalong oil were distilled *in vacuo* at 16 millimeters and gave the following fractions:

No.	Boiling point.	Quantity.	$N\frac{30°}{D}$ properties.
	Degrees.	*Grams.*	
1	Up to 118	20	1.4681 colorless.
2	118–121	62	1.4808 colorless.
3	121–124	65	1.4810 colorless.
4	124–127	63	1.4813 colorless.
5	127–133	58	1.4820 slightly yellow.
6	Residue.	53	Dark, thick resin.

None of the fractions 1 to 5 showed any optical rotation, and united they gave an almost colorless, very fragrant oil, which was completely soluble in 65 per cent alcohol. The resinous residue, saponified with alcoholic potash, gave considerable quantities of higher boiling, fatty acids, and a thick, neutral oil which to judge from the odor, probably contained geraniol. The results of our experiments would seem to show, assuming, as the young leaves contain a higher per cent of oil than the old ones, at least three cuttings of the grass per year, that a yield of from 240 to 300 kilos of oil per hectare can be obtained on good ground in the Philippines. Considering that the demand for this oil is increasing (due partially to the expiration of the ionone patents), I think lemon grass should be considered as a possible catch crop for the first few years of new Philippine plantations. As large stills are necessary, I would suggest that these be built of reënforced concrete on the place. This can be done by any intelligent manager at a much cheaper price than it is possible to purchase metal stills and they can be set up on the ground. For a permanent crop, I do not recommend lemon grass because of the present limited demand for the oil. The grass from which the oil has been distilled is dried and burned under the distilling boilers, and the ashes are distributed over the fields for fertilizing purposes. The exhausted

grass is also used for making paper. The crop is rather an exhausting one for the soil, so that after three years it is usually considered necessary to transplant the grass into a fresh field.

CINNAMOMUM MERCADOI VID.

This large tree, the Tagalog name of which is *calingag,* is very widely distributed throughout the Philippine Islands. The laboratory has botanical collections showing this species of *Cinnamomum* to occur in Davao, Rizal, Pampanga, Bataan, Antipolo, the Camarines, and Tayabas, and it is probably found throughout all parts of the Islands. Tropical forests do not often have many trees of the same species growing together, as is the case with the almost pure stands of the temperate zones, but as many as 150 trees of *Cinnamomum mercadoi* Vid. have frequently been noted on one hectare, and quantities of the bark sufficient for commercial utilization could be obtained if it were of sufficient value. Hence, I obtained 25 kilos of bark from the Lamao region, Bataan Province. This bark was ground and distilled with steam, giving 260 grams (1.04 per cent) of a light yellow oil. The oil had an odor like sassafras and the following properties: Specific gravity, $\frac{30°}{4°}=1.0461$; $N\frac{30°}{D}=1.5270$; $A\frac{30°}{D}=+4°$.

There are no aldehydes in this oil, neither sodium bisulphite nor phenylhydrazine react. I consider that cinnamic adehyde could be detected in this way by distilling a very small percentage in petroleum ether; experiment demonstrated that cinnamic aldehyde instantly gave a crystalline precipitate of the phenylhydrazone with phenylhydrazine.

The oil was distilled at 10 millimeters and gave the following fractions:

No.	Boiling point.	Quantity.	$N\frac{30°}{D}$
	Degrees.	*Grams.*	
1	119–124	77°	1.5333
2	124–130	9.2	1.5320
3	Residue.	11.5	1.5278

Fraction No. 1 redistilled at ordinary pressure had a boiling point 235° to 238° at 760 millimeters; specific gravity, $\frac{30°}{4°}=1.0631$; $N\frac{30°}{D}=1.5335$; $A\frac{30°}{D}=+0.9$. By oxidation with chromic acid this fraction gives piperonylic acid melting at 227°. Piperonal was obtained by heating with alcoholic potash and then oxidizing with potassium permanganate.

These results leave no doubt but that the oil from *Cinnamomum mercadoi* Vid. is almost entirely safrol, and it is remarkable in this respect as most oils from *Cinnamomum* species contain only small amounts of

safrol and large percentages of cinnamic aldehyde. I have also examined two samples of bark of *Cinnamomum* sp. from the Davao region of Mindanao. No sufficient botanical material was sent with these barks to permit the identification of the species, but from the taste and odor of the bark and from the oil obtained by distillation (yield 1.1 per cent) there is little doubt but that they represent the true cinnamon of commerce. Older accounts from Philippine travelers speak of *Cinnamomum zeylanicum* Nees as occurring in Mindanao, and American planters state that the true cinnamon occurs in some quantity in the region back of Davao, and that a small amount of trading in it is carried on among the natives. We have not yet been able to obtain any quantity of this bark or any botanical material for its identification, but expect to be able to do so soon.

PETROLEUM NUTS.

The fruits of *Pittosporum resinifevrum* Hemsl. are known in the Philippines as petroleum nuts, because of a fancied resemblance in the odor of the oil to that of petroleum, and because even the green, fresh fruits will burn brilliantly when a match is applied to them. The tree is essentially an inhabitant of the high mountain ridges, being usually found at an elevation of 500 meters or more. However, one tree was found in Mindoro at an altitude of 170 meters, although it was found in the same region again at 2,500 meters (Mount Halcon). The tree is not very abundant in any part of the Islands, but it is widely distributed, botanical material having been collected from Tayabas, Zambales, Pampanga, Cagayan, Mindoro, Benguet, and Bataan. There is no Tagalog name for the plant as the natives generally do not know the high mountain flora. The oil from the petroleum nut proved to be very interesting as it contained considerable quantities of normal heptane, which has only once before been found in nature, occurring in the digger pine of California, *Pinus sabiniana* Dougl.,[33] and also a dihydroterpene, $C_{10}H_{18}$.

In working up the various lots of *Pittosporum* fruits, considerable differences were noted in the proportions of heptane and dihydroterpene found in the oil, and the season and degree of ripeness of the fruits undoubtedly play a considerable rôle in this respect.

The first lot of nuts was obtained from Baguio, Benguet, in the autumn of 1907. One kilo of whole, fresh nuts gave 52 grams of oil on a press. The residue ground up and again pressed yielded an additional 16 grams of oil; specific gravity=0.883; $N\frac{30°}{D}=1.4577$. It was not possible to determine the optical rotation. The oil is quite sticky, and in a thin layer rapidly becomes resinous. In an open dish it burns strongly, with a sooty flame. It distills unchanged up to 165°, then with decomposition to give a resin oil. The oil distilling from 100° to

[33] *Ann. d. Chem.*, (Liebig), (1879), 198, 364.

165° is colorless, with an orange-like odor; specific gravity, $\frac{30°}{4°}=0.7692$; $A\frac{30°}{D}=+37°.0$. By two careful distillations the following fractions were obtained:

	Fraction (degrees).	Grams.
(1)	98–103	41
(2)	103–110	18
(3)	110–120	21
(4)	120–140	12
(5)	140–150	7
(6)	150–155	47
(7)	155–160	49

Fraction No. 1 had a pleasant odor recalling oranges, and the following properties: specific gravity, $\frac{25°}{4°}=0.6831$; $N\frac{30°}{D}=1.3898$; optical rotation=0.

Fraction No. 7 had a turpentine-like odor. Specific gravity, $\frac{30°}{4}=0.8263$, $N\frac{30°}{D}=1.4630$.

The properties of fraction No. 1 leave little doubt of the identity of this compound with normal heptane.

A second lot of petroleum nuts was obtained in December, 1908, from one of the upper ridges of Mount Mariveles, Bataan Province. One tree gave 15 kilos of fruits, which by pressure yielded 800 cubic centimeters of oil. The residue ground up and distilled with steam yielded 73 cubic centimeters more. This oil distilled in steam contained no heptane, showing that probably all the latter is in the oil cavities immediately surrounding the seeds, and that the pulp of the fruit contains only resins and the higher boiling portions of the oil. It was also noted that the leaves, branches, bark, wood, and in fact, all parts of the tree are distinctly resiniferous and have the same pleasant, orange-like odor as the fruits. The united 873 cubic centimeters of crude oil were slowly distilled at ordinary pressure giving the following fractions:

	Fraction (degrees).	Grams.
(1)	98–110	15
(2)	110–130	13
(3)	130–150	18
(4)	150–160	520

Destructive distillation began above 160°, the temperature of the vapor being from 170° to 240°. The color of the resin oil became continuously darker as the distillation proceeded until near its close, when a light colored oil was collected and the temperature of the vapor fell coincident with a very hot liquid below. The raw oil thus obtained had a light brown color and quite a pleasant odor; specific gravity, $\frac{30°}{4°}=0.978$; $N\frac{30°}{D}=1.4790$; acid number=263. The neutral oil is especially pleasant in odor, recalling that of menthol, although I failed to find this compound.

Thirty kilos of fruits from Baguio, Benguet (December, 1908), were ground and distilled with steam without preliminary treatment with the hydraulic press.

1,350 cubic centimeters of oil were obtained. This was redistilled over sodium and showed about the same relative percentage of heptane and hydropinene as the nuts collected from Mount Mariveles at the same season. (Second lot above.) The Benguet nut is considerably smaller and thinner than that from Mariveles.[34]

All the distillates up to 165° were now united and carefully fractionated ten times, the final result being as follows:

	Fraction (degrees).	Grams.
(1)	97–101	203
(2)	101–120	12
(3)	120–130	8
(4)	130–140	7
(5)	140–150	14
(6)	150–160	600
(7)	Residue, a very resinous oil.	

Fraction No. 1 was shaken out twice with concentrated sulphuric acid and then distilled over sodium, giving 197 grams of an oil, boiling point, 97° to 98°; specific gravity, $\frac{30°}{4°}=0.6752$; $N\frac{30°}{D}=1.3840$; $A\frac{30°}{4°}=0$. The odor is very pleasant, being very much like diphenyl methane. This oil is undoubtedly normal heptane. 125 grams of heptane were treated with 200 grams of bromine in the sunlight. The influence of sunlight on the speed of bromination is very pronounced. It was noted by counting the number of drops of bromine decolorized per minute, that the reaction proceeded about six times as fast in direct sunlight as when the sun was behind a cloud. The principal product of the reaction under these conditions were *n*–heptyl bromide, boiling at 93° at 70 millimeters' pressure, 178° to 181° at ordinary pressure. It gives *n*–heptyl acetate when treated with fused sodium acetate dissolved in glacial acetic acid. This is a liquid of pleasant odor, boiling at 192°.

Fraction No. 6 was distilled three times over sodium and then gave an oil of the following properties: Boiling point, 158° to 160°; specific gravity, $\frac{30°}{4°}=0.8252$; $N\frac{30°}{D}=1.4587$; $A\frac{30°}{D}=29°.6$. The hydrochloride prepared from this oil had the following properties: Boiling point, 114° to 116° at 34 millimeters; specific gravity, $\frac{30°}{4°}=0.9343$; $N\frac{30°}{D}=1.4655$; $A\frac{30°}{D}=+9°$. The reaction of this chloride with magnesium according to Grignard was not very vigorous or complete and therefore the corresponding hydrobromide was prepared and 50 grams subjected to the Grignard reaction, which was quite violent. On treating the product of the reaction with water and dilute acids, a hydrocarbon of the following properties was obtained: Boiling point, 168° to 170°; specific gravity,

[34] In distilling resiniferous oils of the kind under discussion, it is often noted that an emulsion is formed before the liquid has reached the boiling point, the vapor and gas bubbles penetrate this emulsion with great difficulty; they have a fibrous structure, are full of gas bubbles and are so persistent as to be well worthy of note. One of these, while I was heating *Pittosporum* oil in a beaker, was so persistent, that on emptying the contents into a Hirsch funnel, the oil retained the form of the beaker, although on applying a vacuum, it filtered practically clear, with only traces of water and dirt left on the filter paper. These emulsions always disappear as soon as boiling becomes vigorous.

$\frac{30°}{4°}$=0.8050; $N\frac{30°}{D}$=1.4460; $A\frac{30°}{D}$=+1.1. This hydrocarbon is, therefore, hexahydro *p* cymol and the substance found in the oil from the *Pittosporum* fruits is a dihydroterpene $C_{10}H_{18}$.

I performed one experiment in which I subjected the dihydroterpene hydrobromide $C_{10}H_{19}Br$ to the Grignard reaction and heated the reaction product with benzaldehyde for one hour. On decomposing with water and dilute acids, I obtained, besides large quantities of the above hexahydro *p* cymol, a small amount of a crystalline substance melting at 136°, which on analysis proved to be benzoïn, the principal product of the reaction being the reduced hydrocarbon $C_{10}H_{20}$.

0.2032 gram substance gave 0.590 gram CO_2 and 0.1125 gram H_2O.

	Calculated for $C_{14}H_{12}O_2$ (per cent).	Found (per cent).
C	79.3	79.1
H	5.6	6.1

Therefore this reaction corresponds with that of dihydrolimonene magnesium chloride on benzaldehyde under the same conditions.[35]

A low-country species of *Pittosporum*, (*P. pentandrum* (*Blanco*) Merr.) was also examined. This tree is very abundant in the lowlands of all parts of the Islands. Special experiments have shown that it grows vigorously in cultivation. The fruits are quite small, and there is considerable labor involved in gathering them. One tree yielded 16 kilos of fruit which after grinding gave 210 cubic centimeters of an oil of pleasant odor by distillation with steam. The crude oil boiled from 153° to 165° and after being washed with alkalies and distilled over sodium, had the following properties: Boiling point, 155° to 160° (principally 157° to 160°); specific gravity, $\frac{30°}{4°}$=0.8274; $N\frac{30°}{D}$=1.4620; $A\frac{30°}{D}$=40.40.

These properties leave little doubt but that this oil consists principally of the same dihydroterpene that is found in the higher boiling portions of the oil of the ordinary petroleum nut.

VETIVER OIL.

Andropogon squarrosus L. f. (*A. muricatus* Retz.) is native to the Philippines and is found wild and very abundantly in all parts of the Archipelago. It is identical with the *khus-khus* or *khas-khas* of India. I have never seen screens and mats woven from roots in the Philippines as is common in India, but the roots are usually laid away with the clothing to impart to it a pleasant odor. This *Andropogon* is sold in all the larger public markets. The price for small lots is from 15 to 25 centavos, Philippine currency, per kilo. The natives term the roots *moras* or *raiz moras*, and claim that boiling them with vinegar preserves the odor. I was not able to verify this statement by experiments in the laboratory, as it seemed to me that acetic acid simply slightly intensified the apparent

[35] *This Journal, Sec. A.* (1908), **3**, 59.

odor by its own volatility. The experiments conducted in the laboratory on native grass have not yet thoroughly cleared up all points connected with the cultivation and utilization of the roots for perfumery purposes. The yield of roots from various sources and especially the percentage of oil obtainable from them have been very variable. We have now planted on the laboratory grounds in Manila some experimental plots and hope to discover the best methods of handling this crop, as the grass promises to be quite profitable in the Philippines. The oil is valued at 100 to 200 pesos, Philippine currency (50 to 100 dollars, United States currency), per kilo according to quality. The greater part of the distillation at the present time is carried on in Europe from roots shipped principally from India, although some oil is distilled in Reúnion. The plant offers possibilities in the Philippines either for the distillation of the oil or for the export of the dried roots. I am not able to discover that there is at present any exportation of the vetiver roots.

Our experiments on vetiver are as follows:

(1) Thirty kilos of fresh vetiver roots were distilled for two working days (seven hours each) with steam, the condensed water being continually poured back over the roots, and the oil collected in a little petroleum ether to effect easier separation from the water, as the vetiver oil has almost the same specific gravity as water. The petroleum ether was distilled *in vacuo* and there were thus separated 327 grams of a light yellow oil (1.09 per cent) which had a very strong, pleasant odor and the following properties: Specific gravity, $\frac{30^\circ}{4^\circ}=0.9935$; $A\frac{30^\circ}{D}=+32.1$; $N\frac{30^\circ}{D}=1.5212$; saponification number=47.4.

The roots used in the above experiment were obtained from small gardens about Manila and were crushed between the rollers of a sugar mill before being distilled. Such a crushing of the roots seems to improve the yield of oil.

(2) Thirty-one kilos of fresh roots, uncrushed, on distillation as above gave 140 grams oil (0.3 per cent).

(3) Six kilos of dried roots, uncrushed, gave by extraction with ligroin 14 grams of an oil which had only a very slight vetiver odor.

(4) Eighty-one kilos of dry *moras* which had been stored in jute sacks for about three months after harvesting, were distilled with steam with continuous cohobation and yielded 370 grams of oil (0.456 per cent) of an intense odor and brown color. This oil had the following properties: Specific gravity, $\frac{30^\circ}{4^\circ}=0.9964$; $N\frac{30^\circ}{D}=1.5163$; $A\frac{30^\circ}{D}=+32.1$; saponification number=60.6.

It is to be noted that this oil with a higher saponification number has a much stronger odor than that obtained in experiment 1 given above (saponification number=47.4).

(5) A plot of well-fertilized ground containing 150 square meters was planted with vetiver grass. In six months time the plants had flowered and reached maturity; they were then removed, giving 270 kilos of roots, or at the rate of over 18,000 kilos per crop per hectare. However, it was found when these roots were transferred to the laboratory, that they had lost most of their odor, and they gave so small a yield of oil as not to make it worth while to distill them. Some of these plants had been pulled up from time to time and tested for their oil content; they seem to contain the oil up to the time of flowering.

These preliminary experiments seemed to indicate that the proper time for harvesting is about three months after planting, at which time, of course, the yield of roots is not nearly so heavy. The oil in the roots is a protection, and is withdrawn when the plant flowers and seeds. We have planted all of our vetiver by simply burying pieces of divided root tufts in the ground. We have as yet made no experiments on the propagation of the grass from the seed. It was found that the roots can very conveniently be harvested by washing away the soil with a stream of water, catching detached rootlets with a coarse screen. One hundred plants of the above lot, treated in this manner, gave 60 kilos of roots (wet) and 100 plants at Parañaque in a sandy beach soil, gave 23 kilos of roots. The latter were presumably three to four months old and contained a large percentage of oil.

THE COMPOSITION OF VETIVER OIL.

Genvresse and Langlois [36] found in vetiver oil a sesquiterpene, $C_{15}H_{24}$, which they termed vetivene, a sesquiterpene alcohol, $C_{15}H_{24}O$, vetivenol, and an acid $C_{15}H_{24}O_2$. They assign the vetiver odor to an ester of this acid and vetivenol. I am inclined to believe that there may be quite marked differences in the composition of the oil of vetiver due to differences in the age of the roots, methods of storing, distillation, etc., as I have noted that distillates from various lots of roots often had markedly different odors. One oil had very little of the distinctive vetiver odor and reminded me very strongly of gurjun balsam. Another on saponification with alcoholic potash gave large quantities of benzoic acid.

One hundred grams oil (Experiment No. 4) with a strong and pleasant vetiver odor were saponified for one hour on a steam bath with an excess of alcoholic potash. The product was poured into water and separated into neutral and acid products in the usual manner. There were obtained 19 grams of acids, the odor resembling that of fatty acids. The neutral oils retained a very strong odor of vetiver. Purification through the lead salt did not give a crystalline acid, therefore, the acids were distilled *in vacuo*, and after two such distillations gave a 40 per cent yield of a body boiling between 200° to 205° at 4 millimeters' pressure. This acid was a light yellow, viscous oil with a fatty odor like that of oleïc acid. With phenolphthaleïn as an indicator, 1.7850 grams acid required 7.0 cubic centimeters N sodium hydroxide for neutralization, the sodium salt being a noncrystalline, soapy mass; the acid itself had a refractive index, $N\frac{30°}{D}$ =1.4850. This refractive index precludes the possibility of a sesquiterpene acid, as is suggested by Genvresse and Langlois. The analysis is as follows:

(1) 0.210 gram acid gave 0.5730 gram CO_2 and 0.1945 gram H_2O.
(2) 0.1870 gram acid gave 0.5125 gram CO_2 and 0.1650 gram H_2O.

	Calculated for $C_{14}H_{24}O_2$ (per cent).	Found (per cent).	Found (per cent).
C	75.	74.4	74.63
H	10.7	10.19	9.85
Na	9.3	9.0	.....

[36] *Compt. rend. Acad. sci.* (1902), **135**, 1059; *Chem. Ztg.* (1902), **26**, 501.

Titration with potassium permanganate showed that 4.2 atoms of oxygen to one molecule of acid were used in oxidation. The zinc salt was prepared by adding a zinc chloride solution to the solution of the sodium salt. It is insoluble in all solvents. At first this salt precipitates as a gummy mass, which, however, on standing for twenty-four hours in the ice box becomes crystalline.

1.3290 grams substance gave 0.2110 gram ZnO.

	Calculated for $(C_{14}H_{23}O_2)_2Zn$ (per cent).	Found (per cent).
Zn	12.74	12.70

The zinc salt melts at a comparatively low temperature with decomposition to a brown liquid and burns very easily in the air. The lead, copper, silver, and calcium salts are all amorphous precipitates, insoluble in hot water or in alcohol.

The neutral oils were separated into the following three fractions by distillation at 12 to 15 millimeters.

	Fraction (degrees).	Grams.
(1)	125–133	17
(2)	137–140	25
(3)	140–145	22
Residue (semi-solid tar)		17

Fraction No. 1 had no vetiver odor and to judge from its properties is probably a sesquiterpene, identical with the vetivene of Genvresse and Langlois. Fractions (2) and (3) and especially the tarry residue, still had a persistent vetiver odor and the first two in their properties correspond to sesquiterpene alcohols. I expect to make more exhaustive studies on the composition and especially on the best methods of cultivating, storing, and distilling vetiver when more material is available. I consider it doubtful whether the odor of this oil is due to an ester. It is always noted that the odor becomes more marked when a little of the oil is placed in water, and saponified vetiver oils and resinous residues always have this same strong vetiver odor when placed in water. The native practices of both India and the Philippines of wetting the roots to make them exhale their odor are probably due to this fact.

BALAO RESIN.

Balao, panao, or *apitong,* is a soft, semi-solid resin coming from *Dipterocarpus vernicifluus* Blanco and *D. grandiflorus* Blanco. Clover has already made a preliminary report on this resin from this laboratory. The further studies on this subject are given below. The principal present use of *balao* is in the varnishing and caulking of native boats. The *balao* thus used gives a very brilliant, tough and durable coat and would seem to have properties that would make its general use for varnish manufacture desirable. The tree is rather widespread and in many localities quite abundant in the Philippines.

I am informed by Doctor Whitford and Mr. Curran, of the Bureau of Forestry, that there is no question but that very large quantities of

these resins could be gathered if there were a commercial demand for them, and as they do not belong to the present class of varnish gums (fossil resins) the supply would be perpetual. In spite of the advantage which *balao* has in its exceedingly tough, durable, and hard coat, it has the very serious disadvantage of drying very slowly. Thus far I have not been able thoroughly to combine it with linsed oil, turpentine, or with other driers to make a quick-drying varnish. Another suggested use for the resin is for the treatment of gonorrhœa as a substitute for copaiba. A similar, possibly identical, resin is now being shipped from the Malay States for this purpose.

The distillation of *balao* presents some difficulty as there is a considerable quantity of water mixed with the resin, hence a violent foaming occurs on attempting distillation *in vacuo*. On running steam through the viscous resin to remove the volatile constituents, the difficulty is soon encountered that after heating for a short time the whole resin becomes very hard and solid, so that steam does not readily penetrate it. These difficulties were overcome by distillation *in vacuo* from an oil bath with the following arrangement:

Between the air pump and the receiver a three-way stop-cock is inserted. This is arranged to connect the distilling flask with the air pump or with the open air. As soon as the resin threatens to foam, a little air is let in through this stop-cock, and thus, by careful manipulation, it is possible to control the distillation until all the water has passed over, after which time there is no difficulty.

The record of the various experiments made on *balao* resin is as follows:

(1) I attempted to dissolve 270 grams of fresh *balao* resin in 500 cubic centimeters of ether, with the idea that in this manner the water could be removed and the resin easily distilled *in vacuo*. One hundred and ninety grams were dissolved and after drying with calcium chloride distilling off the ether, etc., were added to the filtered oil of experiment (2). The insoluble 80 grams was a hard, brittle, yellowish resin, which proved of value in making varnishes.

(2) One kilogram of *balao* was treated with 2 liters of ligroin (boiling point 60° to 80°). After heating for one hour on a reflux condenser, the solution was filtered. This is a very slow operation, as the paper is clogged by the gummy mass. Two hundred and twenty grams insoluble resin and a little dirt remained on the filter paper. After removing the water, shaking out with alkalies, drying and distilling off the ligroin, there remained 620 grams of the viscous, yellow oil. This was distilled *in vacuo*, and once redistllled *in vacuo* gave 190 grams of an almost colorless oil having the following properties: Boiling point at 10 millimeters' pressure, 120° to 125°; specific gravity, $\frac{30°}{4°}=0.9105$; $N\frac{30°}{D}=1.5014$; $A\frac{30°}{D}=85.8$.

This sesquiterpene is only partially soluble in 95 per cent alcohol. It is not completely miscible with glacial acetic acid. On adding to this mixture a drop of concentrated sulphuric acid, there is obtained a fine, red color, which gradually darkens.

The distillation residue is a hard, yellow, lustrous resin, soluble to the extent of about 75 per cent in alcohol or turpentine, the solutions giving hard, lustrous varnish coatings. This resin dissolves completely in two volumes of linseed oil and two of turpentine, giving a varnish which dries slowly (five days) to a tough, hard coating. The resin was further tested as to its solubility in the following solvents: petroleum ether hot or cold, very slight; cold acetone 75 per cent soluble, no more soluble on heating; almost completely soluble in cold xylol, chloroform, carbon tetrachloride and amyl acetate; in benzol it is but slightly soluble, hot or cold; it is 75 per cent soluble in ethyl acetate and 50 per cent soluble in cold chloral hydrate, the latter solvent taking it up with a red color. It is completely soluble on warming, the color being darker, approaching blue.

(3) Five hundred and seventy grams *balao* resin were carefully heated in a large evaporating dish over a free flame, the temperature being noted by means of a thermometer thrust into the resin. At 100° there was much foaming, due to water separation. The mass was kept at 100° for one hour, then gradually raised from 110° to 120°. Water continued to be given off and there was a very marked thickening of the mass, but no especial evidence of decomposition. In the next half hour, during which time the temperature had risen to 160°, the mass gradually became thicker and more solid, with constant evolution of water. At this stage 75 grams had been lost, and the acid number was 20.0 as compared to 18.6 for the original resins. The corresponding saponification numbers were 25.4 and 23.0. All these differences may readily be credited to the loss of water and show that this heating has no effect on these two factors. The solubility in alcohol seems to be somewhat increased over that of the unheated resin, but this may be due to the water loss. The temperature was finally raised and maintained at 200° to 220° for one hour. The resin melted and on cooling solidified to a hard, brittle, lustrous mass. The loss finally was 240 grams or 42 per cent.

(4) Three hundred grams *balao*, 700 cubic centimeters alcohol, and 50 grams potassium hydrate were heated to 100° for one hour with a reflux condenser. Almost complete solution had taken place upon saponification. The mass was poured into water and separated into neutral and acid portions. Fifty-two grams of solid, crystalline acids were separated from the alkaline extract on treating with hydrochloric acid. These acids were only partly soluble in ether, and this solvent therefore gives a means of separation. The neutral oils were shaken out with ether. At first all were soluble, but after the ether solution had stood for two days, 60 grams of a crystalline solid separated; this was filtered. The ether was then dried and evaporated, whereupon the residual oil distilled *in vacuo* gave 75 grams of sesquiterpene, boiling between 130° and 134° at 15 millimeters, nearly all passing over at 130°; specific gravity, $\frac{30°}{4°}=0.9111$; $N\frac{30°}{D}1.4969$; $A\frac{30°}{D}=+108.7$. There remained in the distilling flask 70 grams of hard, yellow resin with properties similar to those detailed under experiment 3.

(5) Acid and saponification numbers of two samples of *balao*.

	(1)	(2)
Acid number	13.0	10.0
Saponification number	18.5	34.16

(6) A sample of a very liquid *balao* was obtained and the solid constituents were separated from it by using a coarse, muslin cloth for a filter. A thick, viscous oil was obtained having approximately the consistency of castor oil. It had the following constants: $N\frac{30°}{D}=1.5120$; $A\frac{30°}{D}=+33°.1$; acid number=20.8; saponification number=23.6.

This oil, treated with concentrated sulphuric acid, gives a brillant scarlet-red color. It is but partially soluble in a glacial acetic acid, and if a drop of concentrated sulphuric acid is added to this solution, a red color is obtained which in the course of a few minutes becomes darker and changes into an intense purple. With a drop of concentrated nitric acid, the oil only gradually gives this deep purple color, the acid beneath the oil being red.

(7) The product of five trees was caught in small boxes cut in the trees, similar to those used in the turpentine industry of the southern United States. This was done during four days and the total gathered amounted to 1,025 grams with an acid number of 13.4 and a saponification number of 20.9. This resin was white and of the usual consistency. It was thoroughly mixed and 50 grams heated from 200° to 220° in a metal bath with a reflux condenser for four hours. At first there was violent foaming, which soon eeased. The product was very liquid on removing from the hot bath, but on cooling changed to about the same consistency as that of the unheated resin. The hardening noted in other experiments when heat was employed was probably due to the removal of water. The solubility of this fresh resin in various solvents is about the same as that of the older, commercial resins. The product of one tree (40 centimeters in diameter) for five days (320 grams) was also collected. This was an exceedingly fluid resin which gathered in a very liquid state in longitudinal cracks in the heart of the tree. An attempt was made to centrifugate the solid particles from this resin, but there were evidently not sufficient differences in specific gravities to make this operation a success.

(8) *The destructive distillation of balao resin.*—Five hundred grams *balao* resin were distilled from a 1.5 liter Jena flask, a metal bath being used in the first part of the operation. There was slight foaming in the beginning, but after one-half hour, during which time the temperature of the metal bath had risen to 200°, the mass became very thick and gelatinous. Twenty grams of water and 5 grams of oil had distilled. It was now necessary to use a free flame. The whole mass melted, a considerable quantity of water was given off, and a fraction of oil (155 grams) boiling at 253° was obtained, the thermometer remaining practically constant. The next fraction (50 grams) came over very slowly, the thermometer registering 253° to 255°. The temperature of the vapor then began to fall and decomposition set in, as was evidenced by the blue color of the distillate, and the marked darkening of the resin in the flask, by gas evolution, etc. There were obtained 120 grams of a green oil, at a moderate heat, during the next two hours, the thermometer in the vapor showing a temperature of 220° to 230°. The heat was now markedly increased, a 7-inch Bunsen flame playing directly on the flask, and 110 grams of a greenish-brown oil distilled at 290° at 310°. Thirty grams of a black, solid tar remained in the flask. The total time of distillation was four hours. The amount of gas given off during the destructive distillation of *balao* resin is very small.

All fractions were redistilled as follows:

(*a*) The fractions obtained up to the time of decomposition were united, dried with calcium chloride, and distilled *in vacuo*, the boiling point being 128° to 131° at 13 millimeters' pressure, the greater part passing over at 129° and leaving a residue in the distilling flask of 12 grams, which was added to the fraction below. This is termed fraction number 1.

(*b*) The resin oils were redistilled at ordinary pressure, giving two fractions; these are fractions numbered 2 and 3.

(2) 180° to 225°, a light brown oil, 85 grams.

(3) 225° to 310°, a blue, fluorescent oil, 210 grams.

Various determinations were now made upon these three oils by Mr. Mariano Vivencio del Rosario of the Bureau of Science as follows:

No.	Specific gravity, $\frac{20°}{4°}$	Index number.	Saponification number.	Acid number.
1	0.9089	268.3	4.01	1.8
2	0.8882	192.1	10.7	23.0
3	0.9387	120.9	12.75	18.

The properties of the resin oil, fractions (2) and (3) united, were as follows: Specific gravity, 0.9215; index number, 144.6; saponification number, 12.07; acid number, 19.7.

These oils, when extracted with alkali, washed, dried, etc., give a light green, fluorescent oil of a rather pleasant odor.

(9) Many attempts were made to dissolve *balao* resin in linseed oil or turpentine, or to treat it with driers to give a quicker drying varnish.

Balao is completely and easily soluble in hot linseed oil, but on cooling the whole separates out, constituting a jelly which is not very soluble in turpentine. However, if *balao* is heated with linseed oil to 300° for six hours and then two volumes of turpentine added, about 75 per cent of the resin remains in solution and this solution, when filtered, gives a very satisfactory varnish. Additions of lead oxide, lead linoelate, manganese borate to *balao* resin, with subsequent boiling, did not seem to increase the drying properties. Terpineol, in which many unmelted resins dissolve, gave no better results.

THE SESQUITERPENE FROM BALAO RESIN.

I consider that, because of the narrow range of the boiling point of the fraction 128° to 131° at 13 millimeters, an individual sesquiterpene is contained in *balao* resin. Six hundred grams of this sesquiterpene were distilled three times *in vacuo* over sodium, the resulting oil being almost colorless, with the peculiar pleasant odor of the resin, reminding one slightly of oil of cedar. This oil had the following constants:

Boiling point at 8 millimeters, 118° to 119°; specific gravity, $\frac{30°}{4°}=0.9104$; $N\frac{30°}{D}=1.4956$; $A\frac{30°}{D}=+116.4$; ester and saponification numbers=0. Molecular refraction:

Calculated for $C_{15}H_{24}H_2$ (per cent).	Found (per cent).
66.15	65.9

This latter number shows that the sesquiterpene belongs to the bicyclic series, with two double bonds and one bridge bond.

The sesquiterpene, isolated in the manner described above, was now distilled at ordinary pressure; 150 grams of the oil passing over completely between 261° to

262°.4 (standard thermometer, wholly in the vapor). The distillate was yellow in color, being somewhat darker than the oil distilled *in vacuo*, but no odor, gas evolution, or other phenomena which would indicate any decomposition were noted. The constants found were: Specific gravity, $\frac{30°}{4°}=0.9104$; $N\frac{30°}{D}=1.4960$; $A\frac{30°}{D}=+116.5$; $A\frac{30°}{D}=+120.8$.

The action of bromine on the sesquiterpene was as follows: Some of the body of a constant boiling point was mixed with glacial acetic acid in which it is not very soluble. A violent reaction took place on adding bromine drop by drop, and the liquid turned an intense blue color, later passing into purple. As the sesquiterpene is completely and easily soluble in chloroform, the next experiment was made while using this solvent. The same results were obtained. On adding a very dilute, cold solution of bromine in chloroform to a solution of the terpene in chloroform in a freezing mixture, the first few drops were simply decolorized, but very soon the same color changes as have been mentioned above manifested themselves. The brominated sesquiterpene in every instance proved to be a hopeless tar.

A small amount of sesquiterpene gave no reaction either in the cold or at 100° when treated with sublimed aluminum chloride. The oil reacted instantly with warm, acidified potassium permanganate, reducing the permanganate, and giving a tar of a very pleasant odor from which no definite bodies could be isolated. The sesquiterpene when treated with concentrated hydrochloric acid at first gave a pink color which later deepened to an intense purple. Iodine numbers for this sesquiterpene were determined for me by Mr. Reibling and Mr. del Rosario of the Bureau of Science. Working according to the standard Hanus method they found 367, 372, 375, 384 (calculated Hanus number for 61=376). The iodine number which was found, depended upon the length of time during which the sesquiterpene remained in contact with the iodine solutions. If these solutions were left standing for twenty-four hours or more, iodine numbers much higher than the above were obtained, namely, 564, 583, etc. These results are probably due to the peculiar, unsaturated, and easily oxidizable structure of the sesquiterpenes.

Some of the sesquiterpene isolated as described above and which had been allowed to stand in a glass-stoppered bottle in the light for one and one-half years was redistilled over sodium *in vacuo*. It gave the following constants: Boiling point at 15 millimeters, 130° to 131°; specific gravity, $\frac{30°}{4°}=0.9100$; $N\frac{30°}{D}=1.4950$; $A\frac{30°}{D}=101.2$.

This body was dissolved in an equal weight of dry ligroin and saturated with dry hydrochloric acid. Two molecules of hydrochloric acid for one molecule of the sesquiterpene were added and the solution became purple. No solid hydrochloride could be obtained and the addition product could not be distilled *in vacuo* without decomposition. An attempt was therefore made to subject the crude product to the Grignard reaction in the hope that di- and tetra-hydro sesquiterpenes, at present an unknown series of bodies, might be obtained. The hydrochloride had a slight action on magnesium, but as the reaction did not go to completion it was impossible to isolate the compounds wished for. The attempts to prepare these reduced sesquiterpenes, which may throw some light on the very dark field of their chemistry, will be repeated

with cadinene hydrobromide, as we have in the Philippines a large supply of this sesquiterpene obtainable from the oil of *supa*.

THE DISTILLATION OF BLUMEA BALSAMIFERA DC.

Blumea balsamifera DC. grows very abundantly in many parts of the Philippines. I have made a few experiments for the purpose of determining whether this plant can profitably be cultivated and utilized. From 0.1 to 0.4 per cent of a yellow oil with a camphor-like odor is obtained on distilling the leaves. This is almost pure *l*–borneol. As this substance is so easily oxidized to camphor, the oil from *Blumea balsamifera* should be valued at from one-half to three-fourths the price of camphor. The growth of this plant in the Philippines is exceedingly vigorous and the leaves could be cut four times a year. According to some experiments made in Indo-China,[37] it is possible to obtain 50,000 kilos of leaves per hectare, per year, which would give a possible borneol yield of from 50 to 200 kilos per hectare. As labor is not exceedingly cheap in the Philippines, it is a question whether the cultivation and distillation of these plants could be handled at a profit. This would need to be worked out.

THE DISTILLATION OF LANTAVNA CAMARA L.

Lantavna camara L., a sweet-scented weed, is exceedingly abundant in the Philippines. It grows so abundantly and so luxuriantly that if the oil is of any value, its cultivation is certainly a commercial possibility.

Seventy kilos of the leaves distilled with steam gave 60 cubic centimeters of a light yellow oil; 100 kilos gave 245 cubic centimeters, and 110 kilos gave 78 cubic centimeters of oil.

These results show that the yield of oil evidently varies considerably, the differences depending upon the season, age of the leaves, etc. The oil has a specific gravity of $\frac{30°}{4°}=0.9132$; $N\frac{30°}{D}=1.4913$; $A\frac{30°}{D}=+11.5$. Its odor reminds me somewhat of sage. Fifty grams distilled *in vacuo* gave two fractions as follows:

(1) Twenty-two grams boiling between 125° to 130° at 12 millimeters; $N\ \frac{30°}{D}=1.4892$.

(2) Twenty-four grams boiling between 130° and 140° at 11 millimeters; $N\frac{30°}{D}=1.4970$.

We shall send samples to Europe for valuation, and if it proves to be of any commercial value we will study the question further.

OIL OF YLANG-YLANG.

In a previous paper in this series,[38] I published constants on first and second grade, pure ylang-ylang oils of known origin. Various regularities were noted which justified me in stating that first grade ylang-ylang

[37] *Bull. Économ.* (1907), n. s. **9**, 202.
[38] *This Journal, Sec. A.* (1908), **3**, 65.

oils were characterized by a low refractive index, low optical activity, and high ester numbers. I have continued the investigation on this season's distillates of this oil and find exactly the same series of regularities. Acetyl numbers have also been made on these oils, and it will be noted that first-grade ylang-ylang oils are characterized by high acetyl numbers as compared with the second-grade oils. The actual determination of these numbers was made by the method of Zerewitinoff [39] and the results calculated to the usual definition of acetyl number, namely, saponification number of 1 gram of oil after acetylation. The numbers obtained by this method are from 15 to 20 per cent higher than those given by the standard method, due no doubt to the well-known behavior of alcohols like linalool and geraniol toward acetic anhydride.

TABLE III.—*First-grade ylang-ylang oils.*

No.	$N_D^{30°}$	$A_D^{30°}$	Specific gravity, 30° 4°	Ester number.	Acetyl number.
		Degrees.			
20	1.4944	−24.3	0.943	119	203
24d	1.4863	−32.5	0.915	100	177
48	1.4880	−42.5	0.910	90	154
49	1.4935	−35.2	0.930	108	187
53	1.4920	−31.0	0.92	106	180
27	1.4872	−40.0	0.918	109	188
28	1.4877	−44.8	0.914	106	183
29	1.4882	−45.6	0.913	102	196
30	1.4897	−43.1	0.922	107	189
31	1.4868	−44.3	0.916	107	192
32	1.4870	−44.6	0.917	106	181
33	1.4892	−50.2	0.915	102	182
34	1.4880	−51.8	0.908	92	147
35	1.4898	−43.0	0.931	129	214
51	1.4860	−22.0	0.934	126	202
52	1.4860	−31.0	0.929	105	182
55	1.4923	−50.2	0.919	97	177
56	1.4921	−50.3	0.919	97	174
57	1.4924	−50.2	0.918	98	179
58	1.4921	−50.3	0.919	96	172
59	1.4921	−50.0	0.917	96	175
60	1.4924	−50.2	0.918	98	178
61	1.4922	−50.1	0.918	98	178
62	1.4922	−50.0	0.917	97	176
63	1.4923	−50.0	0.919	97	175
64	1.4921	−50.3	0.918	97	176
1	1.4885	−40.0	0.917	102	182
2	1.4880	−40.0	0.910	92	161
3	1.4880	−36.5	0.924	118	201
4	1.4860	−34.0	0.922	120	209
7	1.4910	−43.0	0.932	100	178

Samples 55 to 64 inclusive represent ten distillations made in the same day, using three stills and the same lot of mixed flowers.

[39] *Ber. d. deutschen chem. Ges.* (1901), **40**, 2023.

TABLE IV.—*Second-grade ylang-ylang oils.*

No.	$N_D^{30°}$	$A_D^{30°}$	Specific gravity, $\frac{30°}{4°}$	Ester number.	Acetyl number.
		Degrees.			
21	1.4933	−46.2	0.915	85	132
A	1.4928	−40.4	0.912	86	130
M	1.4923	−38.5	0.914	86	138
L	1.4913	−42.2	0.910	86	127
26	1.4923	−39.8	0.915	88	141
39	1.5014	−79.3	0.910	83	112
40	1.5011	−70.9	0.916	84	108
41	1.5004	−70.4	0.914	83	109
42	1.5010	−74.0	0.912	74	107
43	1.5012	−78.8	0.909	74	104
44	1.5012	−73.2	0.912	85	109
45	1.4922	−39.2	0.912	87	120
46	1.4910	−41.0	0.905	85	124
47	1.4915	−41.0	0.913	85	131
36	1.4990	−71.2	0.905	71	96
37	1.5002	−77.2	0.906	72	101
38	1.5008	−71.9	0.912	74	103
50	1.4910	−43.0	0.910	84	131
54	1.4920	−41.8	0.910	84	127
5	1.5030	−58.7	0.923	80	115
6	1.5005	−49.0	0.925	87	118
8	1.5021	−56.0	0.925	75	110

I have also undertaken the extraction of the perfume oil from ylang-ylang flowers. Many of the constituents of essential oils are very delicate substances and distillation with steam decomposes these compounds to a considerable extent, so that a steam-distilled oil but rarely has exactly the same odor as the flowers from which it was obtained. Extraction with cold solvents and the removal of the solvent *in vacuo*, the temperature never being allowed to rise above 40°, gives oils which have exactly the same aroma as the flowers. This process has the further commercial advantage that such extracted flower oils can not be imitated synthetically, as the change in aroma is undoubtedly due to traces of very easily decomposable compounds which it will be difficult, if not impossible, ever to isolate and identify. The extracted oil need fear no competition with synthetic oils. Alcohol, ether, chloroform, and petroleum ether have been used as solvents for ylang-ylang oil, and the last named has given the best results. Naturally, a very high grade of petroleum ether, which leaves no bad smelling residue when distilled up to 40° in a vacuum of 40 millimeters, must be used as the solvent for the essential oil. Operating in this manner, we have obtained oil yields of from 0.7 to 1.0 per cent. The oil is of a very dark color and contains a considerable amount of resin in solution. When in bulk, the odor is not particularly pleasant or very strong, but when the extract is greatly

diluted the pleasant aroma of the flowers becomes very apparent. The physical constants of one sample of this oil were as follows: Specific gravity, $\frac{30°}{4°}$=0.940; N $\frac{30°}{D}$=1.4920; ester number=135; acetyl number=208.

The oil is too dark to permit readings of its optical rotation to be practicable. These constants are seen to agree quite well with those of a very high grade distilled oil, and as was stated above, the different odor is probably due to traces of delicate compounds present in the extracted oil, which are destroyed during the process of distillation. It is rather curious to note that when this extracted oil is shaken out with water, a considerable amount of resin separates, carrying the distinctive flower aroma, and the separated oil then has an odor resembling that of methyl–*p*–kresol.

These extracted oils should sell for a considerably higher price than the best distilled oils, which fact, taken in consideration with the increased yield and the impossibility of competition from synthetic oils, offers a very attractive new industry to the Philippines.

OTHER PRODUCTS.

The leaves of an unknown species of *Fagara* collected in the northern provinces were examined and found to contain a small percentage of an oil which contained limonene and also probably a limonene derivative which may also be obtained by the action of a solution of dilute, alkaline, copper sulphate on limonene. The compound gives a crystalline derivative with phenylhydrazine and its nature will be taken up in a subsequent publication.

One of the mints, *Hyptis suaveolens* Poir., known by the Tagalog name of *sub-cabayog,* was also examined.

Two hundred kilos of this weed distilled with steam yielded only 27 grams of a greenish oil, with a powerful menthol odor. Investigation proved that menthol was the principal constituent of this oil, but the yield is much too small to render the plant of any value for purposes of distillation.

The leaves of *Clausena anisum-olens* (Blanco) Merr., a tree which is rather abundant in some parts of the Philippines, have an odor which is strongly like that of anise. Alcoholic extracts of these leaves also have a very strong anise-like odor. It is possible that this plant can be used locally in preparing *"anisados,"* which are favorite alcoholic beverages among the natives. It is interesting in this connection to note the statement of Busse,[40] who, speaking of the medicinal and economic plants of Dutch East Africa, states that *Clausena anisata* Willd. does not smell

[40] *Ber. d. deutschen pharm. Ges.* (1904), **14**, 215.

like anise, but like heliotrope. This is not true for the Philippine species of this plant.

There are two varieties of flowers known as *champaca* in the Philippines, the yellow and the white, *Michelia champaca* and *M. longifolia* Bl. Of these the yellow has much the finer odor and it is considered by experts to be by far the finest perfume in the Philippines, the scent being at the same time very soft, strong, and lasting. Small parcels of *champaca* oil, principally distilled from the white variety, have been sold in Europe, the supply coming mostly from Java. The Filipinos are very fond of the flowers, they being made into wreaths and sold in small lots at the rate of a peso to a peso and a half per kilo. One attempt at steam distillation of an oil from the flowers was not successful. The yield of oil was very small and did not have an odor greatly resembling that of the flowers. Enfluerage with paraffine oil has been successfully applied. The paraffine oil is allowed to stand over the flowers for twenty-four hours, drawn off, filtered and made up to the original volume before being applied to fresh flowers. By ten such extractions a very fine, strong odor is imparted to the paraffine which is now suitable as a base for perfumes, or the champaca oil may be extracted from the paraffine with strong alcohol. The loss in paraffine is large, so that we shall endeavor to extract the flowers with petroleum ether, alcohol, ether and other volatile solvents. Very few flowers were available this year because of the many typhoons during the flowering season, which lasts from September to November. The tree is readily propagated from the seeds and begins to bear in three years. The quantity of flowers which can be obtained from one tree is much less than from the ylang-ylang, but the price of champaca extracts is enormously higher than those from the latter.

We have also attempted to obtain a perfume oil from the flowers of *Plumeria acutifolia* Poir., which is used as an ornamental tree in the cemeteries throughout the Islands. The fragrance of the flowers is faint, but characteristic, and the flower is supposed to be the source of the perfume known as "frangipani." I distilled 40 kilos of flowers with steam, but obtained no oil, nor even an aqueous distillate of pleasant odor. Many extraction experiments with different solvents have shown that the perfume is very easily destroyed by heat so that the temperature used in handling these flowers must never rise above 40°. Extraction with low-boiling petroleum ether and distillation of the petroleum ether *in vacuo* gives a gummy oil with a satisfactory odor. The best results which we have obtained thus far are by enfluerage with paraffine oil, the operation being carried out as detailed above under champaca. The season, weather conditions, and time of day seem to have a very pronounced effect on the amount of perfume in these flowers, and we have not yet worked out all these factors.

We have distilled 100 kilos of the roots of *Curcuma zedoaria* Rosc., which is very abundant in many localities near Manila. Sixty-five grams of oil (0.665 per cent) were obtained and also 40 grams of a volatile, beautifully crystalline solid.

The oil has a dark, greenish-brown color and a pleasant, slightly camphoraceous odor. It is probably optically inactive; certainly its optical activity does not exceed $+1°.5$. The oil is so dark as to preclude more accurate measurement. Specific gravity, $\frac{30°}{4°}=0.933$; $N\frac{30°}{D}=1.4920$.

It is readily soluble in two or more volumes of 80 per cent alcohol. On distilling the lowest boiling portions of the oil *in vacuo,* it loses its camphoraceous odor (probably due to cineol) and the scent then becomes quite flower-like. Although oil of zedoary is one of the oldest known essential oils, very little has been discovered concerning its composition. A study of the chemical composition of this oil will be taken up later. It is to be noted that the specific gravity of the oil I obtained does not agree with the figures recorded in the literature for oil of zedoary.

THE OXIDATION OF PHENOL: THE EFFECT OF SOME FORMS OF LIGHT AND OF ACTIVE OXYGEN UPON PHENOL AND ANISOLE.

By H. D. Gibbs.

(*From the Laboratory for the Investigation of Foods and Drugs, Bureau of Science, Manila, P. I.*)

I have shown [1] that neither pure phenol, moist crystals, nor a solution of the crystals in water are affected by the intense sunlight of this locality when exposed in sealed glass tubes in atmospheres of nitrogen, hydrogen, or carbon dioxide.

Kohn and Fryer [2] have exposed both pure phenol crystals and moist phenol *in vacuo* and found the light to have no effect. From these experiments they, and Richardson,[3] conclude that the reactions responsible for the red coloration of phenol are due to hydrogen peroxide oxidation and that the presence of water, oxygen, and sunlight are all necessary factors, the absence of any one of which will prevent the reaction.

These writers, as I have shown,[4] are correct in their opinion that the cause of the red coloration is oxidation and I have isolated the products to be expected from such a reaction, namely, quinone and catechol. Another substance which is probably formed during the reaction is quinol and the presence of the condensation product phenoquinone is extremely probable.

Kohn and Fryer state [5] "since the coloration is always accompanied by the absorption of moisture, the presence of moisture is most probably intimately associated with the formation of the color" and [6] "in the absence of moisture no coloration takes place."

Since writing the first article [7] "The Compounds which Cause the Red Color in Phenol," this phase of the question has been investigated and I find that these statements are not in accord with the facts. It is not surprising that Kohn and Fryer were led into this error, for the character of the sunlight available to them and the atmospheric conditions in their

[1] *This Journal, Sec. A,* (1908), **3**, 361.
[2] *Journ. Soc. Chem. Ind.* (1893), **12**, 111.
[3] *Ibid,* (1893), **12**, 415.
[4] *Loc. cit.*
[5] *Loc. cit.* 110.
[6] *Loc. cit.,* 111.
[7] *Loc. cit.*

locality are hardly comparable with those in which I have worked in the Tropics.

Richardson[8] says: "Dr. Kohn also tells me that a degree of darkening in phenol, such as was obtained by me after three days' exposure in Clifton, England, could only be produced after many weeks under the conditions under which he has exposed it in Liverpool," and Kohn himself remarks[9] that in his own experiments the exposures have been made more under the conditions under which the usual reddening of phenol occurs, the samples being exposed in the south windows of a well lighted room.

I am led to believe that active oxygen in any of its forms will react with pure, dry phenol and consequently produce the coloration. Kohn and Fryer[10] think that the oxidation of phenol goes on in the absence of light and they make the following statement:

"In respect to the action of light a series of experiments showed that the coloration is produced in the dark, although slowly, and therefore the light acts as an accelerator of the change only—an action of which there are many other instances, * * *"

They made exposures of dry phenol in dry air to the light conditions in their locality and found no coloration in seven months. I have, incidental to other work, exposed dry phenol in dry, pure oxygen to the diffused light of this laboratory for several weeks, and moist phenol to moist, atmospheric air in the dark at room temperature for two months without any appreciable coloration becoming visible. Nevertheless, it can not be considered proved that there is no reaction between oxygen and phenol in the dark. In fact it is probable, from considerations which will be advanced later, that a slow reaction takes place.

Hydrogen peroxide reacts readily and I will show, in the experimental part of this paper, that dry ozone is very reactive, either with the pure, dry crystals or with melted phenol. The intimate association of water with the coloration, which Kohn and Fryer observed, is thus explained not as a compound necessary to the reaction, but as one of the products of the reactions:

$$C_6H_5OH+O=C_6H_4(OH)_2,$$
$$C_6H_4(OH)_2+O=C_6H_4O_2+H_2O, \text{ or}$$
$$C_6H_5OH+2O=C_6H_4O_2+H_2O.$$

There is no doubt, however, but that the rate of oxidation is more rapid in the presence of moisture.

Chapman, Chadwick, and Ramsbottom[11] found that the presence of moisture in the reaction between carbon monoxide and oxygen in the presence of ultra-

[8] *Loc. cit.*, 415.
[9] *Loc. cit.*, 416.
[10] *Loc. cit.*, 111.
[11] *Journ. Chem. Soc. London* (1907), **97**, 943.

violet light increases the rate of the formation of carbon dioxide and that while dry carbon dioxide is decomposed by the light, in the presence of moisture no decomposition could be detected. They conclude that in a photo-chemical reaction, the catalyst (moisture) exerts a marked influence in determining the mode of distribution of the energy amongst the molecules of the reacting substances.

EXPERIMENTAL.

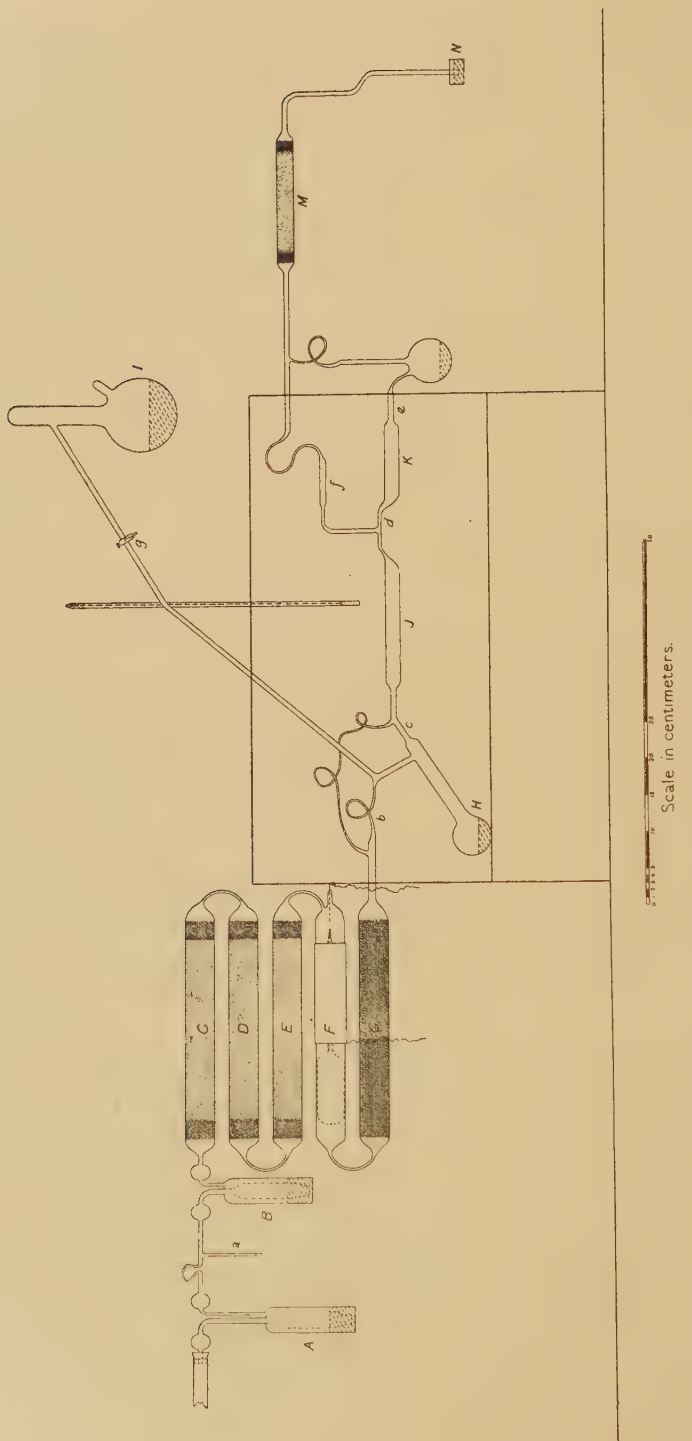
Crystals of purest phenol were placed in a bulb tube and heated in an atmosphere of dry hydrogen until about 75 per cent volatilized. After cooling in the current of hydrogen, this gas was replaced by dry, atmospheric air which had been passed through a purifying chain. The tube was then carefully sealed and placed in the sunlight, at a temperature of about 30°. The crystals colored slowly with liquefaction, until the entire mass had changed into a liquid of a deep red color. The coloration was first noticeable in two hours and liquefaction was complete after about five days, depending upon the quantity of phenol and oxygen present, the size of the tube, the quality of the glass, and some other factors. The experiment and results described were duplicated several times.

This work was then repeated with the utmost care and with an apparatus especially designed to eliminate all known sources of error. It permitted the double distillation of phenol over sodium in an atmosphere of dry, pure hydrogen and the condensation of any desired fraction in two tubes which could be sealed out of the apparatus independently of each other, the replacement of the hydrogen with purified, dry atmospheric air or oxygen, and the treatment of one or both of the tubes with ozonized oxygen in the dark. During all of these operations there was no possibility for the entrance of moisture, for all of that portion of the apparatus between the extremities of the drying tubes at both ends of the chain was composed of glass vessels sealed in a continuous chain.

DESCRIPTION OF APPARATUS. (FIG. 1.)

The gases employed, hydrogen, atmospheric air, and oxygen, were purified by passing through concentrated sulphuric acid, two tubes of calcium chloride, one tube of soda lime, a combustion tube filled with purified asbestos heated to redness, and then into the chain of apparatus shown in fig. 1. Here the gases successively passed through a saturated solution of caustic potash, *A*, concentrated sulphuric acid, *B*, three tubes of phosphorus pentoxide held in place by plugs of glass wool, *C*, *D*, and *E*, an ozonizer of the Siemen's [12] form, *F*, and a tube of tightly packed glass wool, *G*. The next portion of the apparatus consists of an arrangement of tubes and distilling flasks, inclosed in an asbestos oven, for the handling of the phenol, and the tube of phosphorus pentoxide *M*, with its end dipping under mercury in the dish *N* to exclude moisture. All of the apparatus from *A* to *N* was connected by glass seals.

[12] *Ann. d. Phys.* (1857), **102**, 120.


N
M
I
g
f
K
J
H
G
D
E
F
B
A
Scale in centimeters.

DRYING THE APPARATUS AND THE PHENOL.

After the complete chain was closed by glass seals, with the exception of the two extremities and the stopcock *g*, the combustion tube was heated and a slow current of hydrogen passed through for six hours. The portions of the apparatus inclosed in the asbestos oven, shown in fig. 1 by the heavy lines, and also the tubes *F* and *G* were heated to 140° for four hours after which the hydrogen current was stopped and the apparatus allowed to stand for ten days.

A pure sample of about 400 cubic centimeters of colorless phenol was employed as a starting material. It was distilled over a small piece of metallic sodium[13] and the middle fraction collected in a receiver arranged to exclude the light. After cooling, the flask was gently shaken and the crystals which immediately formed represented only about one-half of the total mass, owing to the sudden rise in temperature due to the crystallization of the supercooled liquid. The melted portion was at once drained from the crystals. These were again distilled and the middle fraction collected in the flask *I* through the side tube. A small stick of metallic sodium was dropped in, the side tube sealed, and a slow hydrogen current turned on. The purified sample was again distilled, the first fraction passing out through the tail of the stopcock *g* and the middle fraction condensed in the flask *H* without stopping the distillation, by quickly turning the stopcock. The flask *I* was then removed by sealing the outlet tube below the stopcock *g*.

The asbestos oven was heated to from 160° to 180° in the steady current of hydrogen for two hours, the phenol partly vaporizing and collecting in the receiver *L*. A small flame was then placed under the flask *H* and the phenol boiled until about one-third had passed through the tubes *J* and *K* and collected in *H*. The source of heat was removed from the oven and the phenol condensed in the tubes *J* and *K* until they were about one-third filled. The whole apparatus was cooled in the current of hydrogen and the distilling flask sealed out of the chain by closing the tubes at *b* and *c*. The residue in the distilling flask was colorless.

In order to change the gas in the apparatus and avoid the phenol coming in contact with oxygen which had not been heated (to eliminate the possibility of the presence of ozone) the outlet *a* was opened and the hydrogen in the combustion-furnace displaced by air. The combustion-furnace was again heated, the outlet *a* sealed, and the hydrogen throughout the apparatus displaced by air. The tube *K* was removed by careful fusion at the points *d* and *e*.

The phenol in this tube (*K*) colored gradually when it was placed in the direct sunlight until the oxygen was practically all in combination. On breaking one of the points under water, the amount of oxygen which had combined was shown by the amount of water sucked in. Other tubes sealed in the same way were found to color more or less rapidly depending largely upon the temperature. When cooled by contact with broken ice, the coloration was only visible after several days' exposure to a bright sun. When the temperature was nearly that of the melting point of phenol, the color appeared in from fifteen minutes to

[13] The sodium employed was in the form of sticks inclosed in small glass tubing into which it has been introduced by melting *in vacuo*. Sections of the tube of the desired length were broken and immediately dropped into the distilling flask. By this means sodium of a comparatively pure quality, free from moisture and hydroxide, was obtained.

one hour, probably because minute particles had been melted. Several tubes after exposure were tested for the presence of carbon dioxide by dipping the point under a clear solution of barium hydroxide and allowing a small quantity of the solution to be sucked in. Small quantities of carbon dioxide were indicated in every case. About 2 grams of pure phenol sealed, in a dry, purified atmosphere containing a little more oxygen than atmospheric air, in a 200 cubic centimeter flask with two outlet tubes, was exposed to the direct sunlight for a month and then tested for carbon dioxide by aspirating the gases through a barium hydroxide solution. All necessary precautions to avoid the introduction of the carbon dioxide of the atmosphere were taken. The tips of the outlet tubes of the flasks were not broken until the rubber tube connections were in place, a clear solution of barium hydroxide contained in a *U* tube attached, and soda lime tubes and a wash bottle containing a concentrated solution of potassium hydroxide, to prevent the entrance of carbon dioxide, connected. A considerable amount of carbon dioxide was indicated by the heavy precipitate of barium carbonate.

After the tube *K* had been sealed off, the atmosphere in the apparatus was replaced by pure oxygen, the tube *J* being wrapped in black paper to exclude the light. No coloration of the phenol could be observed. The tube *J* containing the phenol crystals was then packed in broken ice and the oxygen current ozonized by connecting the terminals of the ozonizer *F* with an induction coil. The reaction between the ozone and the cold phenol crystals was at first very slow, no appreciable coloration being visible for several hours. However, when it had begun, the action proceeded with increasing velocity, no ozone escaping from the reaction tube containing the phenol after the reaction was well under way. However, before that time a small quantity of supercooled, liquid phenol farther along in the apparatus, at the point *f*, colored instantly upon the contact with the ozone, but none of the latter escaped at *N*, as was proved by repeated tests. In both cases the first color was bright yellow; this color gradually extended throughout the mass and changed from yellow to pink and finally to a dark, reddish-brown with gradual liquefaction of the crystals.

Another experiment was carried out in the same way, except that the phenol in the tube *J* was not cooled with ice and was in the form of a supercooled liquid. In this instance the phenol colored with great rapidity and no ozone escaped to the tube *f*. The liquid phenol in *f*, in this experiment, was not protected from the diffused daylight of the room, and nevertheless remained colorless after exposure to the rapid current of oxygen throughout the entire experiment which lasted for fourteen days.[14] On bubbling the oxygen escaping at *N* through a potassium

[14] The phenol was subjected to the action of the oxygen current for this length of time for the reason that the ozonizer was rather feeble and produced only a small degree of ozonization.

iodide-starch solution, no coloration was produced, showing that the ozone was entirely removed by reaction with the phenol. Carbon dioxide is given off in considerable quantities during the reaction.

The tube *J* was finally opened and a study of the reaction products made. The reddish-brown liquid was shaken with water, the insoluble portion separated and the aqueous solution extracted repeatedly with chloroform and ether. These extracts were found to contain considerable quantities of unchanged phenol, small amounts of quinone and catechol, and considerable amounts of quinol.

The aqueous solution contained an acid which was volatile with steam, reduced ammoniacal silver solution and mercuric chloride, was precipitated by calcium hydroxide, and on boiling precipitated calcium oxalate. It gave an orange-yellow precipitate with phenylhydrazine[15] in the cold. This precipitate on purification and recrystallization formed yellow crystals. Even though an insufficient quantity of the phenylhydrazine compound was obtained for an analysis, it is reasonably safe to assert that the acid in aqueous solution was glyoxylic acid.

Several experiments were completed in the same manner with the difference that the issuing gases were passed through $\frac{N}{5}$ solutions of barium hydroxide. The following was the result:

	Grams.
Carbon dioxide evolved	0.11
Weight of the mixture in the tube *J* when the evolution of carbon dioxide had practically ceased	3.00
Acidity of aqueous extract was equivalent to 18 cubic centimeters $\frac{N}{10}$=glyoxylic acid (CHO.COOH) equivalent to 4.4 per cent of the residue.	0.13
Chloroform extract	0.64
Ether extract	0.23

The chloroform and ether extracts were dried in a vacuum desiccator with the loss of considerable of the products. The principal loss in weight was due to phenol vaporized.

Two grams of another residue, on distillation with steam gave an acid distillate equivalent to 16 cubic centimeters $\frac{N}{10}$ alkali which, calculated as glyoxylic acid, equals 5.9 per cent.

THE ACTION OF OZONE UPON PHENOL.

Otto[16] observed that ozone reacts with phenol producing a red color. He studied the reaction at 16° and 50° and isolated no reaction products.

Dry ozone is, in general, not reactive. It is more reactive when traces of moisture are present.[17] Pure, dry, ozonized oxygen will react

[15] Fischer, E., *Ber. d. deutschen chem. Ges.* (1884), **17**, 577.
[16] *Ann. chim. et phys.*, Paris (1898), III, **13**, 136.
[17] Uhrig, Richarz, *Phys. Ztschr.* (1905), **6**, 1.

at once with pure, moisture-free phenol in the liquid state and more slowly when the phenol is in the form of crystals. The reactions which take place are largely influenced by the temperature. At the room temperature, 30°, the first action is the production of quinone, and possibly quinol, as indicated by the coloration. As the reaction proceeds an ozonide is undoubtedly produced. This is evidenced by the copious evolution of carbon dioxide and the formation of glyoxylic acid, a reaction analogous to the breaking down of the triozonide of benzene,

$$O_3+3H_2O=2CHO\,.\,CHO+2CO_2+4H_2O,$$

as demonstrated by Harries and Weiss.[18]

When ozone acts upon dry phenol, the water which seems to be necessary to the breaking down of the ozonide, and which also accelerates the reaction, is produced during the formation of quinone as follows:

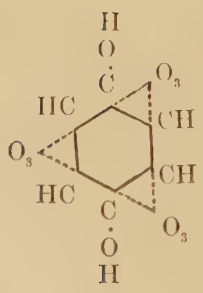
$$C_6H_5\,.\,OH+2O=C_6H_4O_2+H_2O$$

When ozone reacts upon moist phenol, the same reaction products are produced, quinol resulting in larger quantities than quinone.

Whether it is the diozonide of quinone or the triozonide of quinol which breaks down according to the reactions—

$$O_3+2H_2O_2=2HOOC\,.\,CHO+2CO_2+2H_2O$$

or



$$=2HOOC\,.\,CHO+2CO_2+H_2O$$

[18] *Ber. d. deutschen chem. Ges.* (1904), **37**, 3431.

has not been determined. When dry ozone comes in contact with dry phenol, cooled in an ice bath, the velocity of the reaction is very much reduced; the products, however, appear to be the same. Carbon dioxide is evolved and no ozonide can be isolated. No attempts have been made to work at lower temperatures and employ solvents for the phenol, with the view of isolating an ozonide.

THE ACTION OF NASCENT OXYGEN, LIBERATED AT THE ANODE, UPON PHENOL.

By the action of the alternating current upon aqueous solutions of phenol in the presence of magnesium sulphate and magnesium hydrogen carbonate, Drechsel [19] has obtained catechol, quinol, phenolsulphonic acid, γ diphenol, formic acid, oxalic acid, succinic acid and a number of other products. The action of the alternating current in aqueous alkaline solutions has also been studied.

Bartoli and Papasogli [20] have studied the products of the action of the direct current upon alkaline solutions of phenol.

It is to be expected that the oxidation of alkaline solutions of phenol will produce more complicated reaction products than when an acid solution is employed, for the reason that quinone is so easily oxidized to complicated products in presence of alkalies.

EXPERIMENTAL.

A concentrated aqueous solution of phenol, acidified with sulphuric acid to facilitate the passage of the electric current, was divided between two vessels connected by a syphon, and electrolyzed with a direct current passing between platinum electrodes placed one in each vessel.

While the evolution of hydrogen was quite brisk from the cathode, very little oxygen escaped from the anode. The solution surrounding the anode quickly assumed a yellow color deepening to a red, while that surrounding the cathode remained colorless. The anode became coated with a thick layer of a yellowish-red substance which was removed from time to time by washing the electrode in alcohol. This compound is insoluble in water, soluble in alcohol and in phenol, imparting to both solutions a brilliant red color. It is in all probability one of the condensation products to which the coloration of phenol is to be attributed.

The solution around the anode was found to contain considerable quantities of quinone. No complete investigation of the reactions involved was attempted.

THE QUESTION OF THE CHEMICAL ACTIVITY OF OXYGEN GAS IONS.

Experimental data seems to point to the fact that gas ions are not reactive in the chemical sense.

Gockel [21] found that the ionization of ozonized oxygen made by passing oxygen over moist phosphorus was not destroyed by passing the gases through various

[19] *Journ. f. prakt. Chem.* (1884), **2**, 29, 229; and (1888), **2**, 38, 67.
[20] *Compt. rend. Acad. sci.* (1882), **94**, 1339; *Gazz. chim. ital.* (1884), **14**, 90.
[21] *Phys. Ztschr.* (1903), **4**, 602.

solutions, water, potassium hydroxide, dilute and concentrated sulphuric acid, potassium permanganate, pyrogallol, potassium iodide, and oil of turpentine, even though the ozone was in some cases completely removed.

Bredig and Pemsel [22] observed that the rate of the oxidation of sodium sulphite is not accelerated when the air, before passing into the solution, is exposed to the action of ultra-violet or Röntgen rays, uranium or phosphorus. Ewan [23] after studying the slow oxidation of phosphorus, sulphur and aceteldehyde, concludes that in the process only a small portion of the oxygen which is dissociated into its atoms takes part in the oxidation. Van't Hoff [24] in commenting upon the work of Ewan says that the oxidation may be due to oxygen atoms or oxygen ions and that it is not due to ozone. Eder [25] balances the evidence by saying that in the present state of our knowledge it is by no means excluded that oxidation is accelerated by contact of the oxidizable substance with the oxygen which has been ionized by exposure to light and that ozone formation and ionization are accompanying phenomena.

From the experiments performed with the apparatus shown in fig. 1, it is to be concluded that another instance has been added to those above cited, pointing to the inactivity of the oxygen ions in the process of oxidation. By means of this apparatus pure, dry ozonized oxygen was brought into contact with pure, dry phenol in the dark. The tube *G*, containing a length of 18 centimeters of tightly packed glass wool removed the gas ions [26] produced by the brush discharge in the tube *F*, so that it is to be presumed that oxygen in the condition of O_2 and O_3 (and perhaps some atoms due to an equilibrium $O_2 \rightleftarrows 2O$) only pass into the tube *J* containing the phenol. In some experiments the glass-wool filter was omitted from the chain and in others it was in place as shown in fig. 1. In both cases the reaction with phenol in the liquid state, supercooled or not, proceeded at once upon contact with the ozone, no ozone escaping reaction with the phenol, while with phenol which was entirely crystalline the reaction was very much diminished in speed. No variations were noted between the rate or character of the reaction due to the presence or absence of the ion filter in the apparatus chain.

While it is to be concluded from these experiments that ozone is a form of oxygen reactive with phenol, with or without the presence of the gas ions, it is not proved, from the method of experimentation, that the gas ions exert no influence.

[22] Dammer, Handbuch d. anorg. Chem. (1903), 4, 122; Eder, Photochemie, Halle, a/S. (1906), 87; *Jahresb. d. Chem.* (1899), 1, 380.

[23] *Chem. News.* (1894), 70, 90.

[24] *Ztschr. f. phys. Chem.* (1895), 16, 411.

[25] Photochemie, Halle a/S. (1906), 87.

[26] With respect to the removal of the ions formed by the action of Röntgen rays see Thomson and Rutherford, *Phil. Mag. & Journ. Sci.* (1896), 42, 392. With respect to ions formed in other ways see Conduction of Electricity through Gases, 1906, 11. On page 39 Thomson states: "From these numbers we conclude that the ions produced by Röntgen rays, by radio-active substances and by ultra-violet light are identical, a conclusion which we shall find confirmed by several other courses of reasoning."

INFLUENCE OF THE GLASS OF THE CONTAINING VESSEL ON THE RATE OF COLORATION.

Different varieties of glass have been found to show different absortion values to short wave lengths. Atmospheric air is more opaque to the most chemically active ultra-violet rays than fluorspar, rock salt, or quartz.[27]

Phenol exposed to the action of the sun's rays is colored more rapidly under quartz glass than under ordinary glass. A sample of pure phenol was divided into two equal portions in watch glasses, one covered by a clear glass dish and the other by a quartz dish of almost exactly the same thickness, and placed side by side in the sun. The sample protected by the quartz glass distinctly showed more coloration in two hours. After several days the coloration of the two samples was found to have deepened in about the same ratio.

Two small, thin glass bulbs of equal size inclosing equal quantities of phenol, were placed in the sun, one protected by a soda-glass dish and one by a quartz dish. The coloration was noticeably more rapid under the quartz than under the soda glass. Layers of equal thickness showed the difference in color to be marked when viewed through a color comparator.

THE PRODUCTION OF OZONE IN THE SUNLIGHT.

Atmospheric air and oxygen are ozonized by ultra-violet rays.

Lenard[28] has shown that under their influence gases become conducting and in the case of oxygen, ozone is formed. These effects were brought about in air by the short wave lengths to which the atmosphere is comparatively opaque. Lenard's[29] observations that coal gas or an atmosphere charged with coal gas is even more opaque to the short wave lengths than pure air has been confirmed by J. J. Thomson.[30] Regner[31] has found the wave lengths below 200 $\mu\mu$ to be ozone producing, while those above 257 $\mu\mu$ have the opposite effect. Since Meyer[32] observed that the ozone absorption spectrum shows a maximum at wave length 257 $\mu\mu$, it is to be expected that these waves will be most active in the process of deozonization. The oxygen absorption spectrum[33] begins about the wave length 193 $\mu\mu$ and extends farther into the ultra-violet and Lenard[34] found that the region of greatest ozone production lies between the wave lengths 140 to 190 $\mu\mu$.

Since only the absorbed rays produce chemical reactivity it is evident that, as the character of the vibrations changes from the shorter to the longer wave lengths, the ozonization process is changed to one of

[27] Lenard, *Ann. d. Phys.* (1900), **306**, 486.
[28] *Ann. d. Phys.* (1900), **70**, 486.
[29] *Phil. Mag.* (1897), **43**, 254.
[30] *Proc. Cambridge Phil. Soc.* (1908), **14**, 419.
[31] *Ann. d. Phys.* (1906), **325**, 1033.
[32] *Ibid.* (1903), **12**, 849.
[33] Kreusler, *Ann. d. Phys.* (1901), **6**, 418.
[34] *Loc. cit.*

deozonization, the change in wave length producing this effect being about 60 $\mu\mu$; that is, from 193 to 257 $\mu\mu$. The sun's rays being a mixture of wave lengths constantly changing in character as they pass through the earth's atmosphere, the shorter being absorbed, and, as suggested by Fisher and Braehmer,[35] with the formation of ozone, it is reasonable to suppose that the ozonization process gradually changes to one of deozonization as the earth's surface is approached and that greater quantities of ozone are not found near the surface, not so much through the destruction of ozone by oxidation, as Fisher and Braehmer have advanced, as through the influence of the longer wave lengths,[36] the temperature also being an important factor. From the experiments of Regener it may be assumed that there is an equilibrium between O_2 and O_3, at every temperature, and that the concentrations of the molecular oxygen and the ozone depend, other conditions being equal, upon the concentrations or intensities of the various absorbed wave lengths in the rays to which the gas mixture is exposed. Moreover Briner and Durand [37] have found that the temperature is an important factor in this equilibrium. Oxygen, under the influence of the silent discharge, reaches an equilibrium with 11 per cent ozone formation at —78°, while at —194° the conversion to ozone is practically quantitative.

Elster and Geitel found that amalgams of sodium or potassium inclosed in glass vessels loose a negative charge in the daylight. J. J. Thomson,[38] referring to their work, stated that "The glass vessel would stop any small quantity of ultra-violet light which might be left in the light after its passage through the atmosphere." In this reference he must have had in mind the shorter wave lengths, for it can not be doubted but that wave lengths shorter than 300 $\mu\mu$ reach the surface of the earth. Edmond Becquerel,[39] sixty-six years ago, with a crude apparatus and a flint-glass prism, succeeded in photographing the sun's spectrum to about

[35] *Ber. d. deutschen chem. Ges.* (1905), **38**, 2639.

[36] Ozone in the upper atmosphere will be swept to the surface by air currents. The variation in the amounts found in the surface atmosphere may be thus accounted for.

Peyrou (*Compt. rend. Acad. sci.* (1894), **119**, 1206) could find ozone in the atmosphere of Paris only when there were high winds. He, however, rather attributes the results to the circulation of ozone formed over growing crops.

De Thierry (*Ibid.* (1897), **124**, 460) has observed that the quantity of ozone in the atmosphere increases with the altitude. At Chamonix, altitude of 1,050 meters, the amount found was 3.5 milligrams, while at Grands-Mulets, Mont Blanc, altitude 3,020 meters, 9.4 milligrams per 100 cubic centimeters were found.

Hartley (*Journ. Chem. Soc. London* (1881), **39**, 127) states, "The foregoing experiments and considerations have led me to the following conclusions: First, that ozone is a normal constituent of the higher atmosphere. Second, that it is in higher proportion there than near the earth's surface."

[37] *Compt. rend. Acad. sci.* (1907), **145**, 1272.

[38] Conduction of Electricity through Gases, Cambridge Univ. Press (1906), 251.

[39] *Ann. d. chim. et phys.* (1843), III, **9**, 298.

the wave length 328 $\mu\mu$. Photographs made with improved apparatus show the Fraunhofer line *U* which has the wave length 294.8 $\mu\mu$. Since the limit of visual sensibility of the human eye is about 400 $\mu\mu$ (Nutting [40] says 330 $\mu\mu$) the above statement of Thomson can not be considered as being strictly accurate.

It is evident that ultra-violet light will penetrate to the interior of a glass vessel exposed to the sun's rays, the quality of the glass being an important factor. Regener[41] states that glass absorbs the ultra-violet rays below the wave length 300 $\mu\mu$. Fisher and Braehmer [41] have observed that the coloration of manganese glass is produced slowly in the sunlight, more rapidly in high altitudes than in the lowlands, and in a few hours on exposure to the rays of the quartz-mercury lamp, and further that this effect is due in the latter case neither to the cathode nor Röntgen ray, but to the ultra-violet light.[42]

From these considerations one would expect that, under the most favorable conditions, the production of ozone in the atmosphere at sea level would be at a minimum (in the absence of other catalysts than sunlight), while if the atmosphere or oxygen were inclosed in a glass vessel, possibly only traces or none whatever would be produced as a result of the action of the sun's rays and that if an equilibrium between ozone and molecular oxygen is established it will lie at the point where the ozone concentration is extremely minute.[43]

While it is possible that ozone may be produced by radioactivity, since radioactivity is present in the atmosphere and M. and Mme. Curie[44] have found that radioactive barium produces ozone in the air and Richarzy and Schenk[45] have shown that oxygen is ozonized with feebly radioactive radium bromide, it does not seem probable that an equilibrium between the two oxygen states will be seriously affected by this influence, or that it requires serious consideration among the causes which produce the oxidation of phenol.

EXPERIMENTAL.

Two soda-glass tubes, 60 centimeters long and 16 millimeters inside diameter, the glass less than 1 millimeter in thickness, were thoroughly dried and sealed, inclosing an atmosphere of pure, dry oxygen, free from ozone and gas ions and placed in the direct sunlight. The moisture was removed from the tubes by sealing them on to the drying chain (see fig. 1) previously described, at the point *b* and the chain was closed to moisture by a phosphorus pentoxide tube sealed on at the right extremity. All of that portion of the apparatus inclosed between the phosphorus pentoxide tubes was heated to 110° for six hours in a

[40] Bull. Bureau of Standards 1908, **5**, 265.

[41] *Loc. cit.*

[42] Fisher, *Ber. d. deutschen chem. Ges.* (1905), **38**, 946.

[43] Ewell (*Electrochem. & Met. Ind.* (1909), **7**, 23) states that the equilibrium between oxygen and ozone at ordinary temperatures is almost infinitesimal.

[44] *Compt. rend. Acad. Sci.* (1899), **129**, 823.

[45] *Journ. Chem. Soc.* London (1904), Abs. **2**, 399; *Sitzungsber. Akad. d. Wiss.*, Berlin (1904), **13**, 490.

current of oxygen. The ozone was removed from the oxygen by the combustion furnace and the gas ions were destroyed by the tube of tightly packed glass wool *G*.[46] After cooling in the oxygen current and standing eighteen hours, the operation was repeated and the tube sealed out of the chain.

A second tube of the same dimensions was treated in the same way, except that before sealing it was opened just in front of the phosphorus pentoxide tube, the oxygen current running at a fairly rapid rate, and a small piece of cleaned and ignited silver foil inserted. The seal was then made several centimeters back from the opening to avoid the introduction of moisture from the flame of the blowpipe. One end of the tube was wrapped with tin foil for a distance of 5 centimeters and the pieces of silver put into this darkened pocket so that the direct rays of the sun would not strike it.

Silver foil discolors in the presence of ozone;[47] the test, however, is not as delicate as some others.

After four and ten days' exposure, respectively, the tubes were removed from the direct sunlight at 1 p. m. to obtain the maximum sun effect and immediately tested for ozone. The first tube was cooled to produce a slightly reduced pressure in the interior, so that on breaking the tip beneath the surface of a sensitive potassium iodide and starch solution about 2 cubic centimeters were drawn in. This solution was passed repeatedly from end to end of the tube and showed no visible coloration on standing in the dark, after twenty-four hours. The second tube was tested by breaking the tips from both ends and washing out the gas, through the small opening, by means of a stream of pure oxygen. The issuing gas played against a piece of sensitive potassium iodide-starch paper without producing any noticeable discoloration. The piece of silver foil also was without indication of ozone. If active oxygen was formed in the sunlight under the conditions described, the amount was so minute that the delicate tests employed were decidedly negative.

THE EFFECT OF OZONE, AND OXYGEN AND SUNLIGHT UPON THE METHYL ETHER OF PHENOL, ANISOLE.

Anisole is not colored by a rapid current of ozonized oxygen bubbling through it for two days at 30°, or by exposure to direct sunlight in the presence of moisture and oxygen for two months, the temperature occasionally rising above 40°.

No special attempts were made to purify the anisole. A sample which had been in this laboratory for some time was distilled once and the middle fraction employed in the experiments. It remained practically colorless throughout the experiments. The fixation of the labile hydrogen atom of phenol prevents oxidation under the conditions of the experiment.

[46] Thomson and Rutherford, *Phil. Mag.* (1896), **42**, 392.
[47] Thiele, *Ztschr. f. öff. Chem.* (1906), **12**, 11.

THE ACTIVITY OF THE PHENOL MOLECULE.

The measurements of the absorption-spectrum of phenol made by Hartley [48] show a broad absorption band with a maximum at $\lambda=272\ \mu\mu$. The breadth of this band depends upon the concentration. With 1 milligram molecule in 100 cubic centimeters of alcohol the extremities of the band are $\lambda=291.6$ to 243.1 $\mu\mu$ and with 1 milligram molecule in 500 cubic centimeters they are $\lambda=283.5$ to 261.5 $\mu\mu$.

Anisole shows the same absorption band, with the difference that it divides into two bands near the head. This variation shows a marked difference between the constitution of the two compounds which has been traced by Baly and Collie [49] to a certain amount of tautomerism in phenol. The absorption band heading at about $\lambda=277\ \mu\mu$ is characteristic of the labile hydrogen atom. Baly and Eubank state,[50] "These results leave no doubt but that phenol, under these experimental conditions, has not the same structure as anisole, and that the difference is due to the wandering of the labile phenolic hydrogen atom."

The active wave lengths are thus seen to be very close to the limit of the sun's rays which escape absorption in the atmosphere and which are capable of penetrating glass. The fact that the coloration of phenol has been found to be more rapid under quartz than under other kinds of glass is evidence upon this point. The failure of Kohn and Fryer [51] to obtain any coloration of pure phenol is evidently due to the atmospheric conditions in Liverpool. In Manila, where this investigation has been carried on, the atmosphere is free from smoke and very clear at certain seasons of the year. The altitude of the sun is such that the ultra-violet absorption of the atmosphere is less than in Liverpool, even if the atmospheres in the localities were equally clear. Hartley [52] says,

> "I have been led to attribute the limited extent of the solar spectrum, as photographed in London, to the selective absorption of rays by the tarry matters in the smoke of the town's atmosphere, especially since my experience of the extraordinary absorptive power of benzene derivatives."

That the phenol molecule is activated under the conditions of the observations described, appears to be a more reasonable explanation of the phenomenon than that the oxygen molecule is activated by available wave lengths which do not approach the region of the oxygen absorption

[48] *Journ. Chem. Soc. London* (1902), **81**, 929.
[49] *Ibid.* (1905), **87**, 1339.
[50] *Ibid.*, 1348.
[51] *Loc. cit.*
[52] *Journ. Chem. Soc. London* (1881), **39**, 111.

spectrum.[53] Bancroft [54] in expounding the second law of Grotthuss [55] says:

"If the active light is light which is absorbed by the substance to be oxidized and not by the oxygen, then the substance to be oxidized has been made active by the light and the oxygen is the depolarizer. If the active light is absorbed by oxygen and not by the substance to be oxidized, then this latter is the depolarizer and the oxygen is made active by light."

Eder [56] with regard to this phase of the question states that a compound which is acted upon by light absorbs only those vibrations of the light with which its atoms vibrate, or are capable of vibrating, in synchrony. In this way the absorption of the light is connected with the intra-molecular constitution of the compound. The amplitude of the vibrating atoms composing a molecule of a substance sensitive to light may be increased by the light waves vibrating in coincidence, and when a certain limit is exceeded, a breaking of the molecular bonds ensues; that is, photo-chemical decomposition takes place. This effect is well exemplified by certain color substances employed in photography to increase the optical sensibility of the silver salts.[57] Bancroft says,[58] concerning the action of optical sensitizers on photographic plates.

"The theory of Grotthuss enables us to make a definite statement in regard to sensitizers, and one that differs to a certain extent from any of the previous ones. A sensitizer must be a depolarizer, directly or indirectly. It must be a reducing agent in the broad sense of the term or it must be changed into one by the action of light. In either case, the sensitizer is decomposed by the action of light on the sensitized plate;" and "Eder's theory of molecular vibration can not account for Abney's experiment with cyanine plates to which the silver bromide was added after the exposure to light." [59]

The possibility that ozone is formed during the combination of phenol with oxygen is not excluded. From the fact that small amounts of carbon dioxide have been found in the tubes of pure phenol and purified atmospheric air after exposure in the sunlight until the major portion of the oxygen had disappeared, it seems to be quite possible that the sunlight reaction produces in a measure the same products as the reaction between ozone and phenol in the absence of light. It is also possible that a peroxide, other than hydrogen peroxide, is formed during the reaction.

[53] In the case of moist phenol, where there is hydrogen peroxide formation, other considerations enter.

[54] *Journ. Phys. Chem.* (1908), **12**, 258.

[55] *Ibid.*, 212. "The action of a ray of light is analogous to that of a voltaic cell (Grotthuss)".

[56] Photochemie, Halle a/S (1906), 43.

[57] *Ibid.*, 45.

[58] *Loc. cit.* 360.

[59] *Ibid.*, 376.

THE EFFECT OF TEMPERATURE UPON THE ACTIVITY OF THE PHENOL MOLECULE.

Kohn and Fryer [60] have observed that the phenol residues in the distilling flasks are always colored. I have many times observed the same phenomenon on distilling phenol when access to the atmospheric air or oxygen was possible. When the phenol was distilled in an atmosphere of hydrogen with the apparatus shown in fig. 1, the residues were always absolutely colorless when viewed by the eye. No precautions are necessary to exclude light and the phenol in the hydrogen atmosphere will remain colorless indefinitely in the sunlight.

EXPERIMENTAL.

About 50 grams of pure phenol were introduced into a distilling flask which was arranged with a tube reaching to the bottom, sealed in at the top of the neck. The phenol from the time of its purification was protected from the light and from contact with substances which might introduce impurities and the distilling flask was likewise protected from the diffused daylight of the room by asbestos wrappings. No corks or stoppers were used in the distilling flask, glass seals only being employed. The sample was distilled with a current of purified, dry, atmospheric air slowly bubbling through the tube reaching to the bottom of the flask. The air was purified by passing through the purifying chain fig. 1, previously described, with the combustion furnace heated.

The distillation was stopped when about 10 cubic centimeters of phenol remained in the distilling flask. The phenol had been at the boiling temperature twenty minutes, and during this time had assumed a light reddish-yellow color, about the shade usually produced by a few hours' exposure, in contact with atmospheric air, to the sun at a temperature of about 40°. On changing the air current to oxygen and heating to the boiling point the rate of coloration was much more rapid, a brilliant red being produced in a few minutes.

A tube of pure, dry phenol, prepared by the method of distillation in hydrogen in the apparatus described, shown by fig. 1, and sealed in contact with purified atmospheric air, was protected from the action of light by heavy wrappings of tin foil, and placed in a steam bath at 100° in the

[60] *Loc. cit.*, 108, state, "The sample was therefore carefully distilled six times successively from a glass retort and the distillate collected in a glass receiver. The first portion of the distillate was always rejected, and a small residue left in the retort in each distillation. The residue left in the retort always possessed a dark pink tinge, which darkened rapidly on exposure, even in blue glass bottles"; and on page 110, "The combined results of the previous series of experiments show that distillation from glass vessels is really an effectual means for completely purifying phenol. For our further experiments we therefore distilled 'absolute' phenol under the conditions already described, and in order to be well on the safe side fifteen successive distillations were made. The final product, which was quite colorless, melted at 41° C. * * * During the distillations the residue in each case turned pink, and on standing become red."

dark. The steam bath was heated for seven hours a day during six days of the week. The tin-foil covering was carefully removed once a week for the shortest possible length of time, to allow examination of the phenol. At the end of the second week a faint reddish yellow was observed. This color deepened constantly as time proceeded.

The rate of combination of the phenol molecule with oxygen, and consequently the formation of the color will undoubtedly be augmented with a gas mixture containing a higher percentage of oxygen than atmospheric air.

It is evident from these experiments, that for the production of the purest phenol, the distillation should not be conducted with access to oxygen. While the temperature of the phenol is elevated it should come in contact only with an indifferent gas. It is also probable that the combination with oxygen goes on at all temperatures down to the absolute zero, the temperature being an important factor of the rate.

INFLUENCE OF THE ALTITUDE OF THE SUN UPON THE RATE OF COLORATION.

I believe that I have noticed a difference in the rate of coloration of phenol at different seasons of the year. When the sun is directly overhead, which occurs twice a year in this latitude, there is apparently a more rapid production of the red color than when it is in the far south in December and January. This observation is attended by so many factors that it is difficult at this time to make any positive statement. A more complete series of observations and measurements extending over a long period of time will be necessary before any definite results can be obtained.

It is obvious that the rays pass through a thinner layer of atmosphere in reaching the surface of the earth when the sun is in the zenith and therefore the ultra-violet absorption will vary at different seasons of the year, and since the shorter wave lengths undergo refraction to a lesser extent than the longer, a greater proportion of the shorter waves reach the earth's surface when the sun is directly overhead.

It is possible that these considerations produce different light effects in the Tropics, where the sun is sometimes in the zenith, than in the temperate and arctic zones where it never reaches the same condition.[61]

The admirable observations of Cornu have shown that the limit of the sun's spectrum is variable, according to the state of the atmosphere and the altitude of the sun[62] and that the longest ultra-violet spectrum was obtained near noon at the highest elevations.[63]

[61] The attempt to photograph the sun spectrum to shorter wave lengths than any recorded will shortly be made in this locality by the writer.

[62] *Compt. rend. Acad. sci.* (1879), **88**, 1101.

[63] *Ibid.* (1879), **89**, 808.

SUMMARY.

1. Pure phenol remains colorless in the sunlight when in contact with the indifferent gases, hydrogen, nitrogen and carbon dioxide.

2. Pure phenol will become colored in the presence of oxygen.

In the dark the rate is not appreciable at room temperatures. It increases with rise of temperature, can be measured at 100°, and at the boiling point of phenol is fairly rapid.

In the sunlight the rate of coloration is rapid and increases directly with the temperature.

3. The cause of the color is oxidation.

The principal products of the oxidation are quinol, quinone, and catechol. Some carbon dioxide has been found.

The principal colored compounds are probably quinone condensation products. The formation of the intense red condensation product phenoquinone is probable.

4. Active oxygen will unite with phenol with considerable ease and rapidity.

Ozone is very reactive. Quinol, quinone, catechol, glyoxylic acid, and carbon dioxide have been identified among the products of the action with ozone. No ozonide has been isolated.

Oxygen liberated at the anode reacts with phenol. Quinone is one of the reaction products.

5. The experiments argue against the chemical activity of the oxygen gas ions.

6. The glass through which the sunlight acts upon phenol in the presence of oxygen has an influence upon the rate of reaction. Glasses having the most complete ultra-violet absorption retard the reaction in the greatest degree.

7. Ozone could not be detected in pure, dry molecular oxygen sealed in a glass tube and exposed to the sun.

8. The altitude of the sun, the thickness of the atmosphere through which it acts, and the atmospheric conditions undoubtedly influence the rate of the coloration of phenol.

9. The methyl ether of phenol, anisole, is not colored by ozone or oxygen and sunlight.

The fixation of the labile hydrogen of phenol decreases the susceptibility of the compound to oxydizing influences.

10. The reactivity of the phenol molecule is augmented by the absorbed wave lengths at about $\lambda=291$ to 243 $\mu\mu$, and as far as has been observed the same effect is produced by higher temperatures. The oxidation and consequent coloration of phenol goes on under both influences.

11. The purest phenol can only be distilled out of contact with oxygen. Hydrogen has been employed in this work.

ON A RAPID CLINICAL METHOD FOR DETERMINING THE AMMONIA COËFFICIENT OF URINES.

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The ammonia coëfficient of a urine is a number corresponding to the percentage of the total nitrogen which is present as ammonia or ammonium salts. The normal urine of adult human beings has an ammonia coëfficient of 4.1 to 4.64 per cent. This amount may increase in various pathologic conditions until half of the nitrogen in the urine is excreted as ammonia and ammonium salts. Such a condition indicates very serious disturbances in the metabolism of the patient.

The present methods of determining ammonia in the urine are quite tedious; they require a rather long process and considerable apparatus. The usual method employed is the distillation of the urine with a mild alkali (magnesia, sodium carbonate, etc.), the evolved ammonia being absorbed in standard acid and the amount determined by simple titration. The total nitrogen is estimated by the Kjeldahl method or less accurately from a determination of the urea in the urine by decomposition with an alkaline hypobromite. A certain amount of urea is always decomposed by the alkali in the distillation method; this entails the appplication of a correction to the results as obtained by the above process. The value of this correction is usually determined, after the ammonia has been distilled in the manner given above, by adding sufficient water to the liquid to bring it up to the original volume, and redistilling under the same conditions and for the same length of time. If the distillation is carried out *in vacuo* to avoid the decomposition of urea by alkalies, great trouble is often experienced because of the foaming of the urine. It is absolutely impossible to distill some albuminous urines *in vacuo* because of the foaming of the alkaline liquids. The method which I propose is sufficiently accurate for clinical purposes, requires no elaborate apparatus, the actual manipulation requires about three minutes and the whole determination is finished in about thirty minutes. I propose to determine the ratio of ammonia to urea plus ammonia; this, for clinical purposes, represents a sufficiently close approximation to the true ammonia coëfficient. The method does not result in a high degree of

accuracy in this determination, yet I consider that this disadvantage is more than overbalanced by its simplicity.

The present method of determining the ammonia coëfficient in the urine is quite beyond the ordinary practitioner. A high ammonia index of the urine has been used in cases of pernicious vomiting of pregnancy as a safe diagnostic indication that the pregnancy should be terminated. It has been shown very clearly that in many cases a delay of a comparatively few hours in operating involved fatal results. When a patient's life is at stake, it is highly important to have a quick method for making this determination which can be carried out by the physician in his own laboratory. It is also probable that there may be wide variations in the ammonia index of the urine in many pathologic conditions. At the present time this determination is but rarely made on urines, consequently but little is known concerning the number of disturbances in the human organism which may cause a large part of the nitrogen to be eliminated as ammonium salts instead of as urea.

I have sometimes obtained ammonia indices varying as much as 10 per cent from the calculated, in several hundred determinations which I have made to test the method outlined in this paper, using known quantities of urea and ammonium chloride: thus with a true ammonia index of 4 there may be obtained 3.6 to 4.4 per cent. This is a very large error in an analytical determination, but nevertheless at the present time, for diagnostic purposes, an ammonia index of 22 would probably have the same significance as one of 24. When more accurate determinations become necessary this method must be improved.

The proposed method is based upon two well-known reactions. When urea is treated with Millon's reagent (mercuric nitrate in nitric acid solution), it is decomposed to give nitrogen and carbon dioxide and this same reagent has no effect on ammonia or ammonium salts.

As is well known, hypobromites in alkaline solution decompose urea into carbon dioxide and nitrogen, the carbon dioxide being absorded; they also decompose ammonia, liberating nitrogen. The reactions may be represented by the following equations:

In acid solution with mercuric nitrate.—

$$CO(NH_2)_2+3O \longrightarrow CO_2+N_2+2H_2O$$

In alkaline solution with hypobromites.

$$CO(NH_2)_2+3O \longrightarrow CO_2+N_2+2H_2O.$$

$$2NH_3+3O \longrightarrow N_2+3H_2O.$$

$$CO(NH_2)_2+3NaOBr+2NaOH \longrightarrow 3NaBr+Na_2CO_3+N_2+3H_2O$$

$$2NH_3+3NaOBr \longrightarrow N_2+3NaBr+3H_2O.$$

The gas evolved by reason of the action of urea on an alkaline hypobromite solution is nitrogen. Both nitrogen and carbon dioxide are given off by the action of urea on the acid mercuric nitrate solution and as they are evolved in equal volumes, half of the gas obtained is

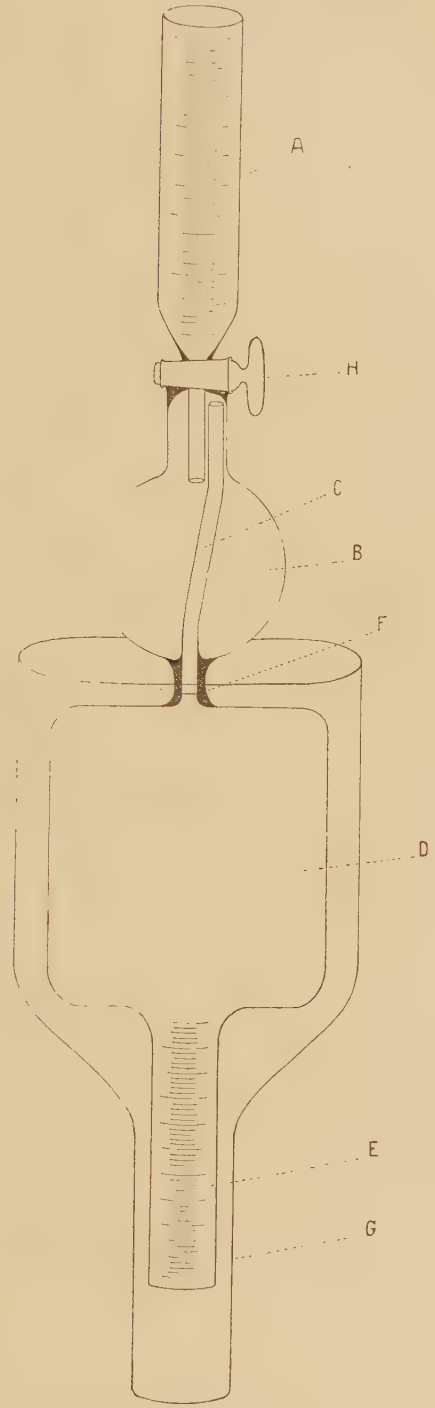

FIG. 1.

nitrogen. Ammonia, as stated above, has no effect on this reagent, whereas with the hypobromite solution the ammonia is also oxidized to nitrogen. Consequently, by oxidizing a solution containing ammonia and urea in two separate pieces of apparatus and noting the amount of gas obtained after the action of each reagent, it becomes a simple matter of calculation to ascertain the respective quantities of urea and ammonia in the original solution. I have devised the following simple form of apparatus for carrying out these determinations. (See fig. 1.)

Two pieces of apparatus are used. *A* is a tube holding 10 cubic centimeters, graduated in 0.1. *B* is a glass bulb having a capacity of 20 cubic centimeters. The tube *C* of about 1-millimeter bore leads from the top of the latter to the graduated eudiometer below. To avoid making the apparatus inconveniently long I have inserted a gas chamber just below the zero mark *F* of the eudiometer; this in the apparatus used with the hypobromite solution has a capacity of 30 cubic centimeters and in the one used with the mercuric nitrate solution one of 60 cubic centimeters. The remainder of the eudiometer *E* is graduated in 0.1 up to 100 cubic centimeters. To measure the gases under the same conditions of pressure, a jacket tube, *G*, of the form shown in the illustration is provided. For the determination in alkaline solution this is filled with water, but for that in acid solution glycerine, mercury, or some other liquid which does not absorb carbon dioxide must be used. Details of the manipulation are as follows:

The mercuric nitrate reagent is prepared by dissolving 10 cubic centimeters of mercury in 130 cubic centimeters of strong nitric acid (specific gravity, 1.4). When solution is complete, 140 cubic centimeters of water are added and, if necessary, the whole is filtered. The reagent keeps well. 10 cubic centimeters of this solution (preferably hot) are run into the bulb *B* of the proper apparatus, the level of the liquid is brought to the zero of the ureometer by raising or lowering the apparatus, and the stop-cock *H* is closed. Then 5 cubic centimeters of the urine (or a sufficient amount of urine to evolve a quantity of gas which will fall on the graduated part of the ureometer) is placed in *A*, and the ureometer is raised until its lower level is just below the surface of the liquid in the jacket *G*. The urine is then run in slowly by opening the stop-cock *H* until only a few drops remain in *A*. Two or three cubic centimeters of water are added to *A* to wash in these last few drops of urine and this is also run into the bulb *B*, care being taken, of course, not to admit any air into *B*. The gas evolution soon begins and may be assisted by shaking the apparatus gently. When the evolution of gas has ceased and the latter has attained the room temperature, the ureometer is lowered until the liquid level is the same inside and outside the eudiometer tube and the gas volume is read. The manipulation with the hypobromite is just the same as with the mercuric nitrate solution, and the urine is added to each solution within a few minutes, so that the gas volumes in both pieces of apparatus may be read off at the same time, both then being under the same conditions of temperature and pressure, no correction is necessary for these factors, as the ammonia index is a percentage coëfficient. The hypobromite reagent is conveniently prepared by adding 1 cubic centimeter of bromine to 10 cubic centimeters of a 20 per cent solution of sodium hydroxide.

In making the calculation of the ammonia coëfficient from the volumes of gas obtained, it is evident that this would be exceedingly simple if the reactions were quantitative. Unfortunately, this is not the case. One gram of urea treated with the mercuric nitrate reagent gives 724 cubic centimeters of the gases, carbon dioxide and nitrogen, instead of the calculated 744 cubic centimeters, an error of 2.67 per cent. One gram of urea with the alkaline hypobromite solution gives only 354.3 cubic centimeters of nitrogen instead of the calculated 372.7 cubic centimeters. I have obtained from one gram of ammonium chloride 208 cubic centimeters of the gas, instead of the calculated 211 cubic centimeters. All these volumes were measured under standard conditions of temperature and pressure, although for the purpose of the determination of the ammonia coëfficient of urine it is not necessary to reduce the volume of the gas to standard conditions. It is only required that the gases in the two ureometers should have the same temperature and be under the same pressure, as the actual quantities of urea and ammonia are not required, but only their ratio. To avoid calculation in the future, I have prepared a table giving the ammonia coëfficient corresponding to various volumes of gases. The number of cubic centimeters of urine plus wash water is subtracted from the observed volume of gas and the ammonia index is then read off directly from the table. The table is calculated by dividing the number of cubic centimeters of gas obtained from the mercuric nitrate solution by 2.05. This number is then subtracted from the number of cubic centimeters of gas liberated from the hypobromite solution, and the ratio of this remainder to the total cubic centimeters of gas from the hypobromite, represents the ammonia coëfficient, as expressed by a formula:

$$A = \frac{\left(H - \frac{M}{2.05}\right) \times 100}{H}$$

Where A is the ammonia coëfficient.

M = number of cubic centimeters of gas from the mercuric nitrate solution.

H = number of cubic centimeters of gas from the hypobromite solution.

TABLE I.—*For calculating the ammonia index of urines.*

Number cubic centimeters gas with mercuric nitrate solution.	Number of cubic centimeters of gas with hypobromite solution.																										
	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	
60	2.6	5.8	8.7	11.5	14.1	16.5	18.8	21.0	23.1	25.1	27.0	28.7	30.4	32.0	33.6	35.1	----	----	----	----	----	----	----	----	----	----	60
61	----	4.19	7.18	10.0	12.6	15.1	17.5	19.7	21.8	23.8	25.7	27.5	29.2	30.9	32.5	34.0	35.4	----	----	----	----	----	----	----	----	----	61
62	----	2.6	5.6	8.5	11.1	13.7	16.1	18.3	20.5	22.5	24.5	26.3	28.1	29.7	31.4	32.9	34.3	----	----	----	----	----	----	----	----	----	62
63	----	----	4.0	6.9	9.7	12.2	14.7	17.0	19.2	21.2	23.2	25.1	26.8	28.6	30.2	31.7	33.2	34.6	----	----	----	----	----	----	----	----	63
64	----	----	----	5.4	8.2	10.8	13.3	15.7	17.9	20.0	22.0	23.9	25.7	27.4	29.1	30.6	32.2	33.6	35.0	36.3	----	----	----	----	----	----	64
65	----	----	----	3.9	6.7	9.7	11.9	13.9	16.6	18.7	20.7	22.6	24.5	26.2	27.9	29.5	31.1	32.5	33.9	35.2	----	----	----	----	----	----	65
66	----	----	----	----	5.3	8.0	10.6	13.0	15.1	17.4	19.5	21.5	23.4	25.1	26.8	28.4	30.0	31.8	32.6	34.2	----	----	----	----	----	----	66
67	----	----	----	----	----	6.8	9.4	11.9	14.2	16.4	18.5	20.5	22.4	24.1	25.9	27.6	29.1	30.6	32.0	33.5	34.8	----	----	----	----	----	67
68	----	----	----	----	----	5.4	8.0	10.5	12.9	15.1	17.2	19.3	21.2	23.0	24.7	26.4	28.0	29.5	31.0	32.4	33.7	35.0	----	----	----	----	68
69	----	----	----	----	----	4.2	6.6	9.2	11.6	13.8	16.0	18.0	20.0	21.9	23.6	25.4	27.0	28.5	30.0	31.4	32.7	34.0	----	----	----	----	69
70	----	----	----	----	----	----	5.3	7.8	10.2	12.6	14.8	16.8	18.8	20.7	22.5	24.2	25.9	27.5	29.0	30.4	31.8	33.1	34.4	----	----	----	70
71	----	----	----	----	----	----	3.9	6.5	9.0	11.3	13.5	16.6	17.6	19.5	21.4	23.1	24.7	26.4	27.9	29.4	30.7	32.1	33.5	----	----	----	71
72	----	----	----	----	----	----	----	5.1	7.6	10.0	12.2	14.4	16.6	18.4	20.2	22	23.6	25.2	26.9	28.4	29.7	31.1	----	----	----	----	72
73	----	----	----	----	----	----	----	3.8	6.3	8.7	11.0	13.2	15.2	17.2	19.1	20.9	22.6	24.2	25.8	27.4	28.7	30.1	----	----	----	----	73
74	----	----	----	----	----	----	----	----	5.0	7.4	9.7	11.9	14.0	16.0	17.9	19.8	21.5	23.1	24.7	26.3	27.7	29.2	30.5	----	----	----	74
75	----	----	----	----	----	----	----	----	3.9	5.1	8.7	11.0	13.1	15.1	17.0	18.9	20.6	22.3	24.0	25.5	27.0	28.5	29.9	----	----	----	75
76	----	----	----	----	----	----	----	----	----	5.1	7.5	9.7	11.9	13.9	15.9	17.8	19.5	21.2	22.9	24.5	26.0	27.4	28.8	30.1	----	----	76
77	----	----	----	----	----	----	----	----	----	----	6.2	8.5	10.7	12.8	14.8	16.7	18.5	20.2	21.8	23.4	25.0	26.5	27.9	29.2	30.5	----	77
78	----	----	----	----	----	----	----	----	----	----	5.	7.3	9.5	11.6	13.6	15.5	17.4	19.2	20.8	22.4	24.0	25.5	26.9	28.3	29.6	30.9	78
79	----	----	----	----	----	----	----	----	----	----	----	6.1	8.3	10.4	12.5	14.4	16.3	18.1	19.8	21.5	23.0	24.5	26.0	27.4	28.7	31.0	79
80	----	----	----	----	----	----	----	----	----	----	----	4.9	7.1	9.3	11.4	13.3	15.2	17.0	18.7	20.4	22.0	23.5	25.0	26.4	27.7	30.3	80

To render this table reasonably compact I have calculated it only for entire cubic centimeters. In the most frequently occurring cases, where fractions of a cubic centimeter of gas are involved, the ammonia coëfficient may be very easily interpolated, from the numbers given in this table.

I also present a table (II) calculated from that of Vanino[1] whereby the actual quantity of urea in a urine may be ascertained from the number of cubic centimeters of gas evolved by the mercuric nitrate solution. To obtain the amount of urea, the number of cubic centimeters of gas obtained is multiplied by the number given in the table corresponding to the temperature and pressure of the gas, thus: if 76.4 cubic centimeters' of gas were found at 25° and 734 millimeters' barometric pressure, the urea amounts to $76.4 \times 1.181 = 0.091$ gram urea.

[1] *Ztschr. f. anal. Chem.* (1895), **34**, 56.

TABLE II.—*Weight in milligrams of urea corresponding to 1 cubic centimeter gas mixture* (CO_2, N_2).

Barometer in mm.	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°	Barometer in mm.
720	1.217	1.212	1.205	1.200	1.195	1.189	1.182	1.177	1.170	1.165	1.158	1.152	1.146	1.140	1.134	1.128	720
722	1.221	1.215	1.210	1.203	1.198	1.192	1.185	1.180	1.173	1.168	1.161	1.155	1.149	1.143	1.137	1.131	722
724	1.224	1.219	1.213	1.206	1.201	1.195	1.189	1.183	1.177	1.171	1.165	1.159	1.153	1.147	1,141	1.135	724
726	1.227	1.222	1.216	1.210	1.204	1.199	1.193	1.186	1.180	1.175	1.168	1.162	1.156	1.150	1.144	1.138	726
728	1.230	1.225	1.220	1.214	1.208	1.202	1.196	1.190	1.183	1.178	1.171	1.165	1.159	1.153	1.147	1.141	728
730	1.234	1.228	1.223	1.218	1.211	1.205	1.200	1.193	1.188	1.181	1.175	1.169	1.163	1.157	1.151	1.145	730
732	1.237	1.232	1.226	1.221	1.214	1.209	1.203	1.196	1.191	1.184	1.178	1.172	1.166	1.160	1.154	1.148	732
734	1.242	1.235	1.230	1.224	1.218	1.212	1.206	1.200	1.194	1.188	1.181	1.175	1.169	1.163	1.157	1.151	734
736	1.245	1.240	1.233	1.227	1.222	1.215	1.210	1.203	1.198	1.191	1.185	1.179	1.173	1.167	1.160	1.155	736
738	1.248	1.243	1.236	1.231	1.225	1.218	1.213	1.206	1.201	1.194	1.188	1.182	1.176	1.170	1.164	1.158	738
740	1.252	1.246	1.240	1.234	1.228	1.222	1.216	1.210	1.204	1.198	1.191	1.185	1.179	1.173	1.167	1.161	740
742	1.255	1.250	1.244	1.238	1.232	1.226	1.220	1.213	1.207	1.201	1.196	1.190	1.184	1.178	1.171	1.166	742
744	1.258	1.253	1.247	1.241	1.235	1.230	1.223	1.217	1.211	1.204	1.199	1.193	1.187	1.181	1.174	1.169	744
746	1.261	1.256	1.250	1.245	1.238	1.232	1.226	1.221	1.214	1.207	1.202	1.196	1.190	1.184	1.177	1.172	746
748	1.266	1.260	1.254	1.248	1.242	1.236	1.230	1.224	1.217	1.211	1.205	1.199	1.193	1.187	1.180	1.175	748
750	1.269	1.263	1.257	1.252	1.245	1.239	1.233	1.227	1.221	1.214	1.209	1.203	1.197	1.191	1.184	1.179	750
752	1.272	1.267	1.260	1.255	1.248	1.243	1.236	1.230	1.224	1.217	1.212	1.206	1.200	1.194	1.187	1.182	752
754	1.276	1.270	1.264	1.258	1.252	1.246	1.239	1.234	1.227	1.221	1.215	1.209	1.203	1.197	1.190	1.185	754
756	1.279	1.274	1.267	1.262	1.255	1.249	1.243	1.237	1.231	1.224	1.218	1.212	1.206	1.200	1.193	1.188	756
758	1.282	1.277	1.271	1.265	1.259	1.253	1.246	1.240	1.234	1.228	1.222	1.216	1.210	1.204	1.197	1.192	758
760	1.286	1.280	1.275	1.268	1.263	1.256	1.249	1.244	1.237	1.232	1.225	1.219	1.213	1.207	1.200	1.195	760
762	1.289	1.283	1.278	1.272	1.266	1.259	1.252	1.247	1.241	1.235	1.229	1.223	1.217	1.211	1.204	1.199	762
764	1.293	1.287	1.285	1.275	1.269	1.263	1.256	1.250	1.244	1.238	1.132	1.226	1.220	1.214	1.207	1.202	764

I have made over two hundred determinations to test the accuracy of this method of estimating the ammonia coëfficient, for the greater part using known quantities of urea and ammonium chloride. A series of these results is given below in Table III. In the determination of the ammonia coëfficient in the urines listed, the figure given under the heading "Calculated" represents the value obtained by determining total nitrogen by the Kjeldahl method and the ammoniacal nitrogen by distillation with powdered magnesia according to the standard method.

TABLE III.

Taken.	Number of cc. of gas with mercuric nitrate reagent.	Number of cc. of gas with alkaline hypobromite.	Ammonia coefficient found.	Calculated.
0.08 gram urea in 5 cc. of water 0.008 gram NH_4Cl in 5 cc. of water	65.0	33.7	5.9	5.6
0.08 gram urea in 5 cc. of water 0.016 gram NH_4Cl in 5 cc. of water	61.0	33.5	10.4	10.6
0.1 gram urea in 5 cc. of water 0.05 gram NH_4Cl in 5 cc. of water	75.0	47.5	21.6	23.5
0.1 gram urea in 5 cc. of water 0 025 gram NH_4Cl in 5 cc. of water	77.0	43.0	12.8	12.4
0.1 gram urea in 5 cc. of water 0.03 gram NH_4Cl in 5 cc. of water	77.5	44.8	14.7	14.2
0.1 gram urea in 5 cc. of water 0.04 gram NH_4Cl in 5 cc. of water	77.2	45.9	18.1	18.3
0.1 gram urea in 5 cc. of water 0.01 gram NH_4Cl in 5 cc. of water	78.1	40.3	5.45	5.6
0.1 gram urea in 5 cc. of water 0.01 gram NH_4Cl in 5 cc. of water	76.2	39.1	5.0	5.6
0.1 gram urea in 5 cc. of water 0.05 gram NH_4Cl in 5 cc. of water	76.0	47.8	22.1	23.5
0.1 gram urea in 5 cc. of water 0.06 gram NH_4Cl in 5 cc. of water	76.8	50.0	25.0	24.9
0.1 gram urea in 5 cc. of water 0.07 gram NH_4Cl in 5 cc. of water	76.8	52.8	29.0	28.1
0.1 gram urea in 5 cc. of water 0.08 gram NH_4Cl in 5 cc. of water	77.2	54.0	30.4	31.0
0.1 gram urea in 5 cc. of water 0.09 gram NH_4Cl in 5 cc. of water	77.0	57.0	33.6	33.4
0.1 gram urea in 5 cc. of water 0.1 gram NH_4Cl in 5 cc. of water	77.5	59.6	35.8	35.2
0.1 gram urea in 5 cc. of water 0.1 gram NH_4Cl in 5 cc. of water	77.5	60.0	36.4	35.2
0.1 gram urea in 5 cc. of water 0.1 gram NH_4Cl in 5 cc. of water	76.1	59.4	37.5	35.2
Fresh normal urine 5 cc	38.0	17.8	4.3	4.1
Urine very much decomposed, 5 cc	20.3	17.9	44.4	45.9
Fresh normal urine 5 cc	64.2	32.8	4.5	4.1
Do	69.4	35.4	4.5	4.1
Urine 24 hours' old, 5 cc	57.2	30.3	7.6	7.2
Urine 72 hours' old, 5 cc	52.4	32.1	20.6	19.9

TABLE III—Continued.

Taken.	Number of cc. of gas with mercuric nitrate reagent.	Number of cc. of gas with alkaline hypobromite.	Ammonia coefficient found.	Calculated.
Urine, pregnancy case	31.4	16.6	7.8	7.2
Urine pregnancy case, duplicate determination. Urine 3 hours older, no new Kjeldahl made on this one	32.9	17.4	8.0	7.2
Urine, fresh normal	65.0	33.3	5.1	4.6
Urine, fresh normal, duplicate	65.5	33.6	4.8	4.6
Urine about 1 week old	34.6	23.1	26.8	26.0
Urine about 24 hours' old	51.0	26.7	6.7	6.3

Now that a very simple and quick method has been worked out, I expect to determine the ammonia index of a great number of urines from persons suffering with various diseases. The results will be published later.

EDITORIAL

THE TENSILE STRENGTH OF MACHINE- AND HAND-STRIPPED ABACA FIBER.[1]

Promoters of hemp-stripping machines have from time to time maintained that the hand-stripped fiber is not as strong as the machine-stripped hemp. It is of considerable importance to the Manila hemp industry to substantiate these claims, as there seems to be little doubt but that in a few years a large part of the abacá leaves will be stripped by machines, and if the machine-stripped hemp is stronger than the hand-stripped variety, the whole Manila hemp industry will be very materially benefited. The present active competition which Manila hemp must meet with the sisal and maguey fibers is largely due to the fact that these latter are machine-stripped, and consequently more uniform and stronger than retted or hand-stripped fibers of the same species.

I have made tests on the comparative tensile strength of machine- and hand-stripped abacá fibers. In the first series of tests, stalks from the same plantation of the same age were selected at random, one-half were stripped on the machine and one-half by hand. The latter represented the best grade of hand-stripping, with a smooth-edged knife, and the resulting hemp was much cleaner than that usually found in the market. While the above method of selection would not be rigid without a very large number of tests, still the results obtained so markedly and uniformly point in the same direction that little doubt is left as to the relative strength of the fibers. In making the tests, ten fibers at one time were twisted together and the number of kilos necessary to break them measured with a Riehle testing machine. Fifty lots of ten fibers each of hand- and machine-stripped hemp of the same length were then weighed to obtain the average weight of the fibers, so that any differences in breaking strain could not be ascribed to different sizes of the fibers used. An arbitrary strength factor X was then calculated, representing the breaking strength divided by the weight of the fibers. The results of the first series of tests are presented in Table I.

[1] These tests were made possible through the kind coöperation of Mr. M. A. Clarke, the machine used being that of the Manila Hemp Machine Company.

TABLE I.

Class of fiber.	Breaking strength in kilos.	Class of fiber.	Breaking strength in kilos.
Mindoro machine-stripped	21.4	Davao machine-stripped	31.4
Do	23.8	do	33.6
Do	24.0	do	31.0
Do	22.6	do	34.5
Do	[a]34.0	Mindoro hand-stripped	14.5
Do	24.1	do	18.6
Do	25.0	do	16.3
Do	21.8	do	14.1
Do	24.5	do	[a]20.4
Do	26.9	do	14.5
Do	22.3	do	15.4
Do	27.6	do	14.1
Do	28.1	do	12.7
Davao machine-stripped	32.6	do	17.7
Do	34.0	do	13.2
Do	35.5	do	14.1
Do	40.5	do	15.4

[a] Picked samples.

The averages for the first series of tests are as follows:

Class.	Number of determinations.	Breaking strength in kilos.	Average weight of 10 fibers in grams.	Strength factor, X.
Mindoro machine	13	25.3	0.0509	50
Mindoro hand	13	15.4	0.0510	30
Davao machine	9	35.4	0.0716	48

In the second series of tests each leaf was split into two parts, one-half was stripped by machine and the other half by hand. This lot of hemp was from Albay Province. The numbers opposite each other represent the same leaf, and hence are comparable. The results are presented in Table II.

TABLE II.

Breaking strength in kilos.		Breaking strength in kilos.	
Machine-stripped.	Hand-stripped.	Machine-stripped.	Hand-stripped.
26.8	11.4	17.8	11.8
19.9	14.0	19.5	10.9
23.4	14.4	21.8	18.2
22.3	10.9	20.9	7.2
21.0	11.4	27.3	11.8
23.1	10.9	16.8	11.4
26.4	13.2	16.8	11.8
19.1	8.6	[a]21.0	[a]12.2
16.8	11.8		
15.0	8.6		

[a] Averages.

The average weight of the two classes of fibers in this last series was the same, so that their relative tensile strength is correctly given by the average breaking strain.

Many other determinations with the same results have been made. There is little doubt but that the machine-stripped fiber is very considerable stronger than the hand-stripped variety. To give a reason for this difference is another matter. Examination under the microscope showed that both classes of fibers were quite clean and revealed no differences between them. It is my opinion that the difference is due to the continuous, steady pull of the fiber under the machine's knife as compared to the intermittent jerky pull which is necessary in hand stripping. The jerks of the hand-stripper strain the fibers so as very markedly to lower their tensile strength. Confirmatory evidence for this theory is given by the fact that hand-stripped hemp shows very many broken fibers, so that a bundle of this class of abacá consists of a series of shorter and longer fibers, while the machine-stripped abacá has practically no fibers broken and all are of the same length. The advent of the hemp-stripping machine should very materially advance the quality of Manila hemp.

RAYMOND F. BACON.

THE EXCRETA OF THE PYTHON.

The Biological Laboratory of this Bureau has one young python, the excreta of which I have examined. This python is now about 18 months old. It is 2.4 meters long and is already so strong that it is very difficult for one man to handle it. This snake eats on an average once in eight days, the meal consisting of one large guinea pig or two rats. It may perhaps be of interest to note that none of the pythons in captivity in Manila must be forced to eat, as is often the case in colder climates.

The excretum is passed two days after feeding as a white, slightly moist solid, accompanied by a considerable quantity of water, which carries most of the mineral constituents in solution. Ten grams of the solid portion of the excreta, dried *in vacuo,* lost 10.3 per cent water. Ten grams of dried excreta distilled with sodium hydrate gave 0.87 gram of ammonia and 8.9 grams uric acid. The calculated amount of ammonia for 8.9 grams uric acid, to form ammonium acid urate is 0.899. The solid excreta of the python are, therefore, almost pure ammonium acid urate.

RAYMOND F. BACON.

A RUBBER VINE.

The woody, climbing vine *Parameria philippenensis* Radlk, is very abundant in the Philippines. The bark of this vine contains a rubber-like gum, which, however, does not flow sufficiently upon tapping to obtain it in that manner. There is such a large quantity of this vine in the Islands of Mindoro and Cebu that at various times companies have been formed to exploit this product commercially as a rubber-yielding plant. At the present time, the bark, which in Tagalog is called *tagulaoay,* is macerated with coconut oil or some other fatty oil, and the resulting thick solution of the gum is used by the natives in treating wounds, the solution acting like surgeon's plaster. It is claimed that by its use infection is absolutely prevented. This was the only disinfectant carried by the Filipino insurgent armies and was used entirely to prevent infections of wounds during the Philippine insurrection. Whether or not it has any value for these purposes can not at present be stated. Analyses of the bark show that it contains from 4 to 5 per cent of this rubber-like gum. Several experiments were made on methods looking toward its extraction on a large scale. The bark of the vine is easily ground to a coarse powder, from which gasoline extracts practically all the rubber. A sticky, greenish, resinous mass was obtained on distilling the gasoline. It was not in this manner possible to obtain a rubber which was not decidedly tacky. Carbon bisulphide gave better results, the rubber being strong and not sticky. The freshly extracted rubber is yellow, but it soon turns black in the air and becomes somewhat tacky. Our experiments seem to show that the commercial utilization of the *Parameria* vine as a source of rubber is very doubtful. Much more can be expected from the rubber gum from the various species of *Ficus,* which is one of the most abundant trees in the Islands. We will soon take up a study of these *Ficus* rubbers.

RAYMOND F. BACON.

NOTE ON THE ACTION OF SODIUM ALCOHOLATES ON ALCOHOLS.

Guerbet[1] has recently published results which demonstrate that when sodium benzylate is heated with members of the lower series of fatty alcohols from 200° to 220°, the hydrogen in the alcohol is substituted by a benzyl group. Thus, with ethyl alcohol he obtained the alcohol $C_6H_5 . CH_2 . CH_2 . CH_2 . OH$, etc. When he substituted aromatic al-

[1] *Compt. rend. Acad. sci.* (1908), 146, 1405.

cohols for the aliphatic he obtained hydrocarbons. Thus, for example, with benzyl alcohol and sodium benzylate, he did not obtain phenyl benzyl carbinol, but stilben, diphenyl, and toluol. The publication of these results induces me to call attention to some experiments made in connection with my studies on sodium benzhydrol and sodium benzylate.[2] I have found by many experiments in which I heated sodium benzhydrol with methyl and ethyl alcohol to between 250° and 300° in sealed tubes that it was not possible to substitute hydrogen in these alcohols under the given conditions. There were obtained with ethyl alcohol and sodium benzhydrol, instead of the expected diphenyl propyl alcohol the following: Benzol; diphenyl methane; sodium benzoate; tetraphenyl ethylene and ethane; ethylene; ethyl ether, and acetaldehyde condensation products; in other words, simply the decomposition products, at this temperature, of sodium benzhydrol and of sodium ethylate. It would also seem theoretically improbable that $\gamma\gamma$ diphenyl propyl alcohol could be formed at this temperature, for the very similarly constituted benzhydrol very readily decomposes at 300°. The results of Guerbet are self-evident from the work of Nef on sodium alcoholates, and from my work on sodium benzhydrol and sodium benzylate. The methylene hypothesis of Nef, assuming an equilibrium between di- and tetra-valent carbon, is not only a very satisfactory explanation for the chemical behavior of alkyl halides and of metallic alcoholates, but makes it possible to predict with a considerable degree of accuracy the reaction between these compounds under various conditions. Fromm[3] obtained symmetrical tetraphenyl butane as one of the products of the dissociation by heat of benzyl sulphide. According to the theory of Nef, this must have been formed by the addition of phenyl methylene to dibenzil, the latter resulting from the union of two phenyl methylene particles and the subsequent reduction of the stilben, thus formed, these reactions are represented by equations as follows:

(1) $(C_6H_5CH_2)_2S \longrightarrow C_6H_5CH< + H_2S$

(2) $2C_6H_5 . CH< \longrightarrow C_6H_5 . CH : CH . C_6H_5$

(3) $C_6H_5CH : CHC_6H_5 + H_2S \longrightarrow C_6H_5 . CH_2 . CH_2 . C_6H_5 + S$

(4) $2C_6H_5 . CH< + C_6H_5 . CH_2 . CH_2 . C_6H_5 \longrightarrow$ $\begin{matrix} C_6H_5 . CH_2 & H_2C . C_6H_5 \\ | & | \\ C_6H_5 . C\text{———}C . C_6H_5 \\ H & H \end{matrix}$

To confirm this method of the formation of symmetrical tetraphenyl butane I chose the benzyl ester of an acid which on decomposition would yield products which could reduce the stilben first formed in the reaction,

[2] *Am. Chem. Journ.* (1905), **33**, 68.

[3] *Ber. d. deutschen chem. Ges.* (1903), **36**, 534.

as special experiments showed that the heat dissociation of benzyl benzoate yielded principally tetraphenyl ethylene, and no symmetrical tetraphenil butane. To this end I heated two molecular quantities of benzyl chloride with one molecular amount of anhydrous potassium oxalate in a sealed tube from 160° to 200° for four hours. I obtained thus a 28 per cent yield of symmetrical tetraphenyl butane melting at 255°. This is the best method thus far suggested for preparing this hydrocarbon.

RAYMOND F. BACON.

REVIEW.

Soils and Fertilizers. By Harry Snyder. B. S. Third edition. Cloth. Pp. xv+350. Price, $1.25 net. New York: The Macmillan Company, 1908.

This book is primarily intended as a text and manual for agricultural instruction. It presents in a brief but comprehensive form the physical and chemical principles of the science. Only one chapter is devoted to the physical properties of soils; this seems rather too brief in view of their relative importance. The chapters on chemical composition of soils, fertilizers, soil preparation, and crop rotation are especially complete and should prove valuable not only to the student in the classroom, but to the practical agriculturist as well.

Much of the subject matter discussed, particularly the questions of soil nitrogen and humus, is based upon the author's extensive work in this field of investigation, hence the facts are presented in a very convincing manner.

The most important features of the work from the students' standpoint are the chapters on laboratory practice and the review questions.

The only reference throughout the book to the effect of climatic conditions on soil fertility is to the checking of nitrification by cold and strong sunlight, with the consequent general tendency to less soil nitrogen in southern latitudes. As the book is not written to meet the demands of tropical conditions, this can not be considered as an adverse criticism.

The book is especially well illustrated throughout.

G. F. R.